EFFECTS OF USING ARSENIC-IRON SLUDGE IN BRICK MAKING

By

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A thesis submitted to the Department of Civil Engineering of
Bangladesh University of Engineering & Technology, Dhaka in
Partial fulfilment of the requirement for the degree

of

MASTER OF SCIENCE IN CIVIL ENGINEERING
(ENVIRONMENTAL)

Department of Civil Engineering
Bangladesh University of Engineering & Technology

July, 2003

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DECLARATION

I hereby declare that the research work reported in this thesis has been performed by me and this work has not been submitted elsewhere for another purpose, except for publications.

28 July 2003

(Md Abdur Rouf)

ACKNOWLEDGEMENT

The author wishes to express his immeasurable and deepest gratitude to Dr Md Delwar Hossain, Professor, Department of Civil Engineering, Bangladesh University of Engineering and Technology (BUET) for his constant support and guidance during the course of this research work starting from, development of the thesis proposal till writing of this thesis. His careful reading of the draft, valuable comments, criticism and constructive suggestion immensely contributed to the improvement of the thesis work.

The author expresses his profound gratitude to Dr A.B.M Badruzzaman and Dr Md Ashraf Ali, Department of Civil Engineering Department, Bangladesh University of Engineering and Technology (BUET) for their sympathetic cooperation and invaluable guidance in successful completion of this research work.

The author is also grateful to the Civil Engineering Department, Bangladesh University of Engineering and Technology (BUET) for having provided him with all the facilities and equipment of Environment Engineering Laboratory, Soil Engineering Laboratory, Strength of Material Laboratory and Concrete Laboratory, which enabled to carry out the research work smoothly.

Profound thanks to Mr Abdur Rahman and all members of environment engineering laboratory for their services and support during the course of this research work.

The author wishes to thank officer in charge and all the members of Manikganj Iron and Arsenic Treatment Plant for assisting him in collection of sludge from sludge bed.

The author also expresses his sincere thanks to all post graduate students involved with International Training Network (ITN) project work for their advice and relentless support in the post graduate research laboratory in carrying out TCLP and column leaching experiment.

Lastly the author also wishes to express heartfelt thanks to members of his family, colleagues and friends for their constant encouragement and overall gratefulness to almighty Allah, Who is the Owner of all praise, for successful completion of the work.

ABSTRACT

Arsenic-iron treatment plants generate huge amount of sludge. The accumulation of these materials is not only burden to the treatment plant but also affects the environment adversely. Therefore, development of new technologies to recycle and convert waste into reusable materials is critically important for protection of environment and sustainable development of society. There is a strong demand for environmentally safe reuse and effective disposal methods of iron and arsenic contaminated sludge out of water treatment plant due to the increasing amount of sludge generated by the water treatment plants in Bangladesh. A possible long-term solution appears to be recycling of the sludge and using it for beneficial purposes.

The study work has been performed to study and analyse the effects of using arsenic-iron sludge in making of bricks. Leaching of arsenic from brick manufactured out of arsenic-iron sludge was investigated with a view to assessing its environment quality. TCLP test of sludge indicated that leaching of arsenic from sludge is more than that of burnt bricks. Increasing the firing temperature resulted in decrease in leaching of arsenic. However, leachate concentrations of bricks manufactured at varying temperature indicate it to be independent of temperature and mix proportion. As leachate from arsenic laden sludge out of Column Leaching method reflects values higher than 5 mg/L; as such indicates it to be toxic waste.

The results of compressive strength tests on the bricks indicate that the strength is greatly dependent on the amount of sludge in the brick and the firing temperature. The optimum amount of sludge that could be mixed with clay to produce good bonding of bricks was 15% by weight firing at 1000^0C. The recommended proportion of sludge in brick making is 15% to 25% by weight and fired at 1000^0C to 1050^0C to produce a good quality brick. It was revealed that addition of sludge up to 25% by weight retain the original characteristics of normal clay bricks. Further, leaching of arsenic is largely reduced when sludge mix is burnt at high temperature in the brick making process.

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LIST OF ABBREVIATIONS

AAS – Atomic Absorption Spectrophotometer

AASHTO – American Association of Standard Highway and Traffic Organisation

ASTM – American Standard of Testing and Materials

BDS – Bangladesh Standard

BUET – Bangladesh University of Engineering and Technology

C – Centigrade

cm – Centimeter

DF – Dilution Factor

DOE – Department of Environment

DPHE – Department of Public Health Engineering

DSMA – Di-Sodium Methylarsonate

DTP – Dual Treatment Plant

Fig – Figure

GF – Graphite Furnace

GFAAS – Graphite Furnace Atomic Absorption Spectrophotometer

kg – Kilogram

LL – Liquid Limit

MSMA – Monosodium Methylarstone

OMC – Optimum Moisture Content

PI – Plasticity Index

PL – Plastic Limit

PZC – Point of Zero Charge

SAM – S – adenosylmethionine

SSA – Specific Surface Area

TCLP - Toxicity Characteristics Leaching Procedure

Temp - Temperature

UF – Ultra Filtration

USEPA – United States Environment Protection Agency

UV – Ultraviolet

WHO – World Health Organisation

wrt – With Respect To

ZHE – Zero Headspace Extractor

CHAPTER 1: INTRODUCTION

1.1 GENERAL

The serious arsenic problem in Bangladesh has led to massive concerted efforts of NGOs and donor agencies in mitigating the crisis. Most of the focus has been on awareness building and the development of water treatment system removing arsenic from drinking water. The disposal of arsenic rich sludge generated from the treatment processes is one of the issues that have received little attention from the sponsors of the technologies and the users (Eriksen et al., 2001). Different treatment technologies are available at present, which may offer solutions to this menace. Among them arsenic removal by coagulation and co-precipitation (Alum Coagulation and Iron Coagulation) and sorption (Activated Alumina, Iron Coated Sand and Ion Exchange Resin) techniques are well-known systems. In arsenic affected areas where the contents of naturally occurring iron and or manganese in groundwater is high, one may be tempted to remove arsenic together with iron and manganese by using the co-precipitation technique. The co-precipitation (Iron-Manganese removal) process produces sludge with considerable arsenic content of up to 10% by weight (Pal, 2001). No proper disposal method for the highly toxic arsenic sludge waste has been developed yet. Uncontrolled disposal of the arsenic sludge may lead to the pollution of the surface water and ground water system and create serious problem for the environment. Different researcher like Pal (2001) emphasised on safe disposal of arsenic contaminated sludge.

There is a strong demand for environmentally safe reuse of and effective disposal methods for iron and arsenic contaminated sludge out of water treatment plant due to the increasing amount of sludge generated by the water treatment plants in Bangladesh. At present, 18 number of large scale Arsenic and Iron Treatment Plant are in Bangladesh. Each treatment plant treat 400 m^3 ground water per hour and generates about 1700-m^3 arsenic rich sludge in a year (DPHE, 2002). While landfills are commonly used for disposal of sludge in Bangladesh, rapid urbanization has made it increasingly difficult to find suitable landfill sites (Lin et al., 2001). At places, it is disposed off to nearby rivers or low laying areas, which is likely to pollute surface and groundwater.

As environmental regulations become more stringent and volume of sludge generated continues to increase, traditional sludge disposal methods are coming under increasing pressure to change. Incineration is costly and may contribute to air pollution and landfill space is becoming scare. A possible long-term solution appears to be recycling of the sludge and using it for beneficial purposes. One technique that is available to treat hazardous waste is solidification that stabilizes and solidifies components of waste. The solidified product is disposed off to a secure landfill site or it can be recycled as construction material like bricks if it meets the specific strength requirement and can be shown to leach toxic pollutants within acceptable limits (Rahmat, 2001).

1.2 OBJECTIVE OF THE STUDY

(a) To assess the environmental viability of stabilisation of arsenic and iron present in water treatment sludge with clay mix.

(b) To assess the effect of this disposal option on strength of brick.

(c) To propose an acceptable clay mix using optimum sludge (arsenic and iron) that can be used as brick aggregate; leading a way to environmentally friendly recycling of toxic solid wastes.

1.3 METHODOLOGY

Raw materials (Arsenic and Iron sludge) were collected from Manikganj Arsenic and Iron Treatment Plant. Upon collection, sludge sample was oven dried for 24 hours at 105^0C. Basic physicochemical characteristics, including moisture content, pH, and organic compound were analysed. Heavy metal content i.e. Arsenic, Iron, Lead and Chromium were determined by acid digestion with a HNO_3: HCl volume of ratio of 1:3 followed by analysis using GFAAS. The Toxicity Characteristics Leaching Procedure (TCLP) in accordance with USEPA Method 1311 was used to determine toxic characteristics of sludge.

A clay sample of normal bricks was collected from the Mirpur Ceramic Factory area. Upon collection, it was grind with a crushing machine. Because water content is an important factor affecting the quality of the brick, tests including Specific Surface Area (SSA) analysis, Atterberg's limits and AASHTO (1982) were conducted to obtain the plastic nature of the sludge-clay mixture and to establish the optimum moisture content (OMC) in the brick making process. Using this OMC, the mixtures with various proportions of sludge (5%, 15%, 25% and 50%) and clay was prepared in batches (3 samples for each proportion). After 24 hours natural drying followed by another 24 hours at 105^0C oven-drying period, mixtures were heated in Carbolite heavy-duty furnace (muffle furnace) at the design temperatures of 950^0C, 1000^0C and 1050^0C respectively for 6 hours. Leaching test of all these burnt samples were carried out by TCLP in accordance with USEPA Method 1311 and long time leaching by column leaching with varying extraction fluid i.e. BUET tap water, rain water and distilled water with phosphate/ sulphate/ nitrate/chloride.

Total 15 bricks sample (length 12.25 cm, width 5.85 cm and height 3.81 cm) of sludge-clay mixture in varying proportion (5%, 15%, 25% and 50%) at OMC were prepared in the laboratory. A clay only mixture sample was prepared as a reference specimen. All these samples were heated in Carbolite heavy-duty muffle furnace at the design temperatures of 950^0C, 1000^0C and 1050^0C respectively for 6 hours. The produced bricks then received a series of tests including firing shrinkage, weight loss on ignition, water absorption and compressive strength, to determine a suitable condition for producing qualified bricks. Flow chart of the experimental procedures for this study is shown in Fig.1.

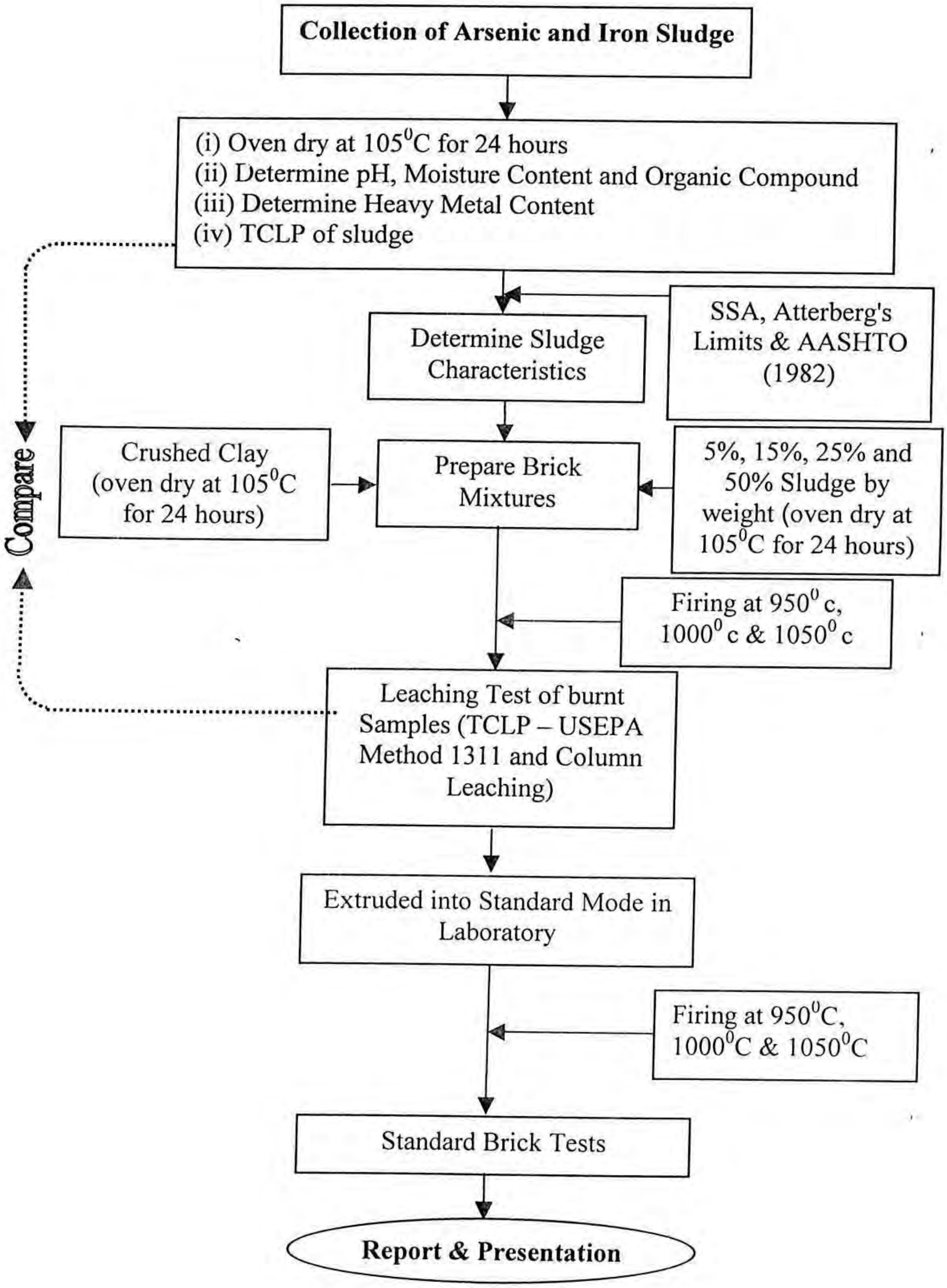


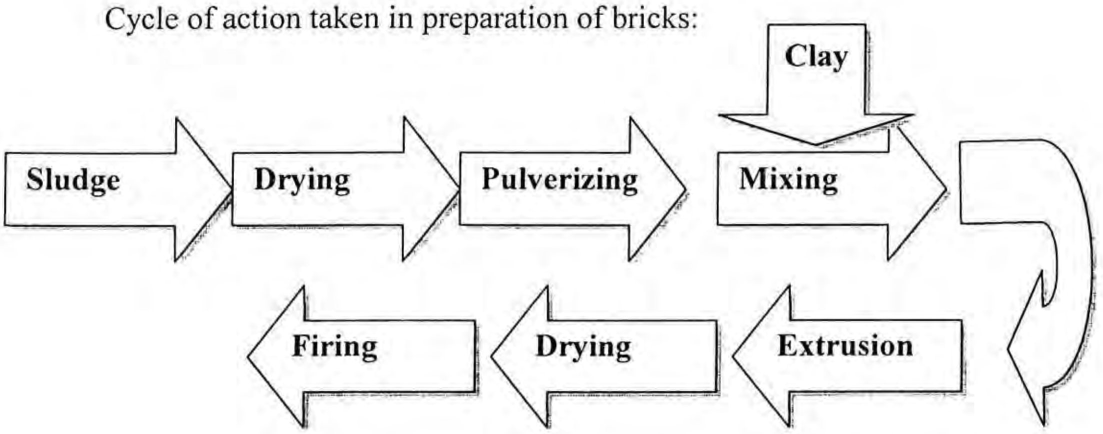
FIG.1. Flow Chart of Experiment

1.4 SCOPE OF THE THESIS

Sludge is an inevitable waste from wastewater or water treatment process. Disposal of sludge has always made-up a substantial portion of the treatment cost. Restriction on sludge disposal practices, such as landfill method has created a need for cost effective alternative due to growing environmental concerns and land space limitations. Conversion of sludge to constructional material is one of the potential options of reuse for sludge.

In this study arsenic-iron sludge out of water treatment plant has been selected as waste material. Sludge has been collected from Manikganj Iron-Arsenic Treatment plant (18 DTP Plants) out of many other types of treatment plant. Hence, characteristics and behaviour of sludge from different types of treatment plant might vary with the process described in this paper. Bricks prepared from sludge–clay mixtures were prepared in laboratory condition. As such standard and quality of bricks prepared in the field (brick field) following the same procedure under natural condition may vary with the brick prepared in the laboratory.

Cycle of action taken in preparation of bricks:



Benefits out of recycling:

- # Eliminate sludge disposal problems.
- # Convert waste into quality products.
- # Create a new reserve of materials.

1.5 ORGANISATION OF THE THESIS

Apart from this chapter, the remainder of the thesis has been divided into seven chapters. Chapter 2 titled "Iron and Arsenic in the Environment" (literature review) presents an overview of chemistry of arsenic and iron in the environment, its mobility in the environment and treatment processes.

Chapter 3 titled "Characteristics of clay and iron-arsenic sludge" precisely describe about physical and chemical characteristics of clay and sludge. It also amplifies the effects of sludge-clay mixtures at varying proportions.

Chapter 4 titled "Standard bricks tests" outline various physical bricks test following BDS: 1980. These tests include compressive strength, firing shrinkage, loss on ignition, water absorption and density of bricks.

Chapter 5-titled "Leaching test of burnt bricks and sludge by toxicity leaching procedure" highlight about standard laboratory method of determining toxicity level with respect to USEPA regulatory value and mass balance analysis.

Chapter 6-titled "Column leaching of sludge –soil mix" describes about long leaching effect of sludge and clay at different anion media condition i.e. BUET tap water, extraction fluid containing phosphate, nitrate, sulphate and chloride anions.

Finally chapter 7 presents major conclusions of the study and also provides recommendations for future study.

CHAPTER 2: IRON AND ARSENIC IN THE ENVIRONMENT

2.1 ARSENIC

2.1.1 GENERAL

Arsenic is a naturally occurring element that is tasteless and odourless. As a compound of underground rock and soil, arsenic works its way into groundwater and enters food chains through either drinking water or eating plants and cereals that have absorbed the mineral. Daily consumption of water with greater than 0.01 mg/l of arsenic, less than 0.2 % of the fatal dose, can lead to problems with the skin and circulatory and nervous system. If arsenic builds up to higher toxic levels, open lesions, organ damages, neural disorders and organ cancer, often fatal, can result (Pal, 2001). Arsenic (As) is a semi metal (metalloid) or transition element belonging to the 5th group of the periodic system of elements with an atomic mass of 74.9216 g/mol. 245 arsenic bearing minerals are known in nature, 4 modifications of elementary arsenic, 27 arsenides (like Nickeline, Lollingite, Safflorite, Rammelsbergit), 13 sulphides (Arsenopyrite, Realgar, Enargite, Orpiment), 65 sulphonamides, 2 oxides, 11 arsenites, 116 arsenates (Mimetasite, Erythrine, Annabergit) and 7 silicates, which when subjected to weathering can release soluble arsenic into natural waters.

Arsenic forms no single cations but reacts readily to inorganic acids or, depending on pH, to the corresponding salts. Until 1973 it was only possible to determine total arsenic. Then Braman & Foreback introduced the first hydride generation technique enabling the determination of inorganic As (III) and As (V) compounds. Dissolved arsenic (V) is sorbed very effectively on iron, manganese and aluminium oxides or hydroxides as tubewell as on clay minerals and organic matter. This is explained by the fact that within natural pH ranges from 4 to 9 As (V) occurs as negative charged H_2AsO_4- or $HAsO_2$- complex which easily reacts with charged surfaces. Also the formation of earth alkaline metal – arsenate (V) complexes as limiting mineral phases, which readily precipitate when supersaturated, can keep arsenic concentrations on a certain level. Lime addition e.g. has been proved to be beneficial in reducing arsenic mobility due to the formation of low-solubility calcium arsenates. Within the average pH range of groundwater from 4 to 9 dissolved arsenic (III) will occur mainly as neutral H_3AsO_3 complex and will therefore undergo no sorption or exchange processes. It is about 4 to 10 times more soluble and mobile as arsenic (V). The most important natural attenuation process known for inorganic As (III) compounds is the precipitation as arsenic sulphide (As_2S_3). Far less tubewell known and less often determined than inorganic compounds are organic compounds, which typically make up 10-20% of the total arsenic, but can also, be as high as 70%. Catalysed by fungi or bacteria a transformation of these inorganic acids to organic acids or depending on pH to the corresponding salts is possible. This process is called "methylation" since one or more OH-groups are replaced by CH_3- ("methyl")-groups. Organic acids in the environment are known with one to three methyl groups, while the existence of Tetra Methyl Arsenic Acid $(CH_3)_4As^+$ is proved so far only in human fabric (Friedrich, 2001).

2.1.2 THE BEHAVIOUR AND FATE OF ARSENIC

Arsenic is a natural constituent of the earth's crust, found commonly in the form of sulphide minerals in association with copper, lead, silver or gold. From its origins in bedrock, arsenic can enter the environment through both natural processes and human activity. Volcanoes release major quantities of arsenic, by weathering of arsenic-containing minerals and ores, and from forest fires. Arsenic is also released through the combustion of fossil fuels, especially coal; from wood preservation industries; from the smelting of sulphide minerals including copper, lead, and zinc; and from gold processing. Once in the atmosphere, arsenic can travel great distances as dust and be chemically altered before returning to the surface of the earth in rainfall. Soluble forms of arsenic in water tend to be quite mobile, while less soluble forms tend to attach to clay or other soil particles and then rapidly enter sediments. Microorganisms in soils, sediments and water produce organic forms of arsenic. Because it is volatile, organic arsenic can renter the atmosphere and ultimately change back into inorganic forms (Enviro Facts, 2002). Environmental substrates show a wide range of arsenic concentration due to the variation of natural and anthropogenic inputs. Average arsenic concentration in the earth's crust is 3 ppm, but the concentration varies from 0.1 to several hundred ppms, depending on the type of rocks (Cullen and Reimer, 1989). Arsenic content in soils is usually 5 ppm to (Baker and Chesnin, 1975) to 6 ppm (Bowen, 1979) but the level may be much higher in soils contaminated by human activities (Hung Yan-chu, 1994). In nature, arsenic goes through the reactions of oxidation – reaction, precipitation- dissolution, adsorption –desorption and organic and biochemical methylation. These reactions control the mobilization and bioaccumulation of arsenic in the environment.

There is a general agreement that most anthropogenic input is due to smelting operations and fossil fuel combustion, but still unresolved is the extent to which human activities contribute to the overall arsenic cycle (Edlestein, 1985). Fig 2.1 shows a simplified, comprehensive cyclic of transfer of arsenic (Bhumbla and Keefer, 1994). The presence of arsenic in igneous, metamorphic and sedimentary rocks generally results in its presence in the water phase. Arsenic concentrations in some minerals, for instance, arsenic readily substitutes silicon, trivalent iron and aluminium in crystal lattice of silicates minerals (Onishi and Sandell, 1955). Concentration of arsenic tends to be high in volcanic glass, aluminisilicate minerals and igneous rocks containing iron oxide. Sedimentary rocks generally contain higher concentration of arsenic than igneous and metamorphic rocks. Arsenic in non-marine shales/clays has been adsorbed by clay minerals, whereas arsenic associated with marine shales/clays is present in pyrites and organic matter (Tourtelot, 1964). High arsenic concentrations in phosphate have been positively correlated with the organic and the iron content of the rock (Stow, 1969). The capacity of sediment to retain and concentrate arsenic is primarily controlled by grain size (Horowitz, 1984). Any retention of arsenic by soils would occur by adsorption, especially if the soils contained iron or aluminium oxides (Livesey and Hung, 1980).

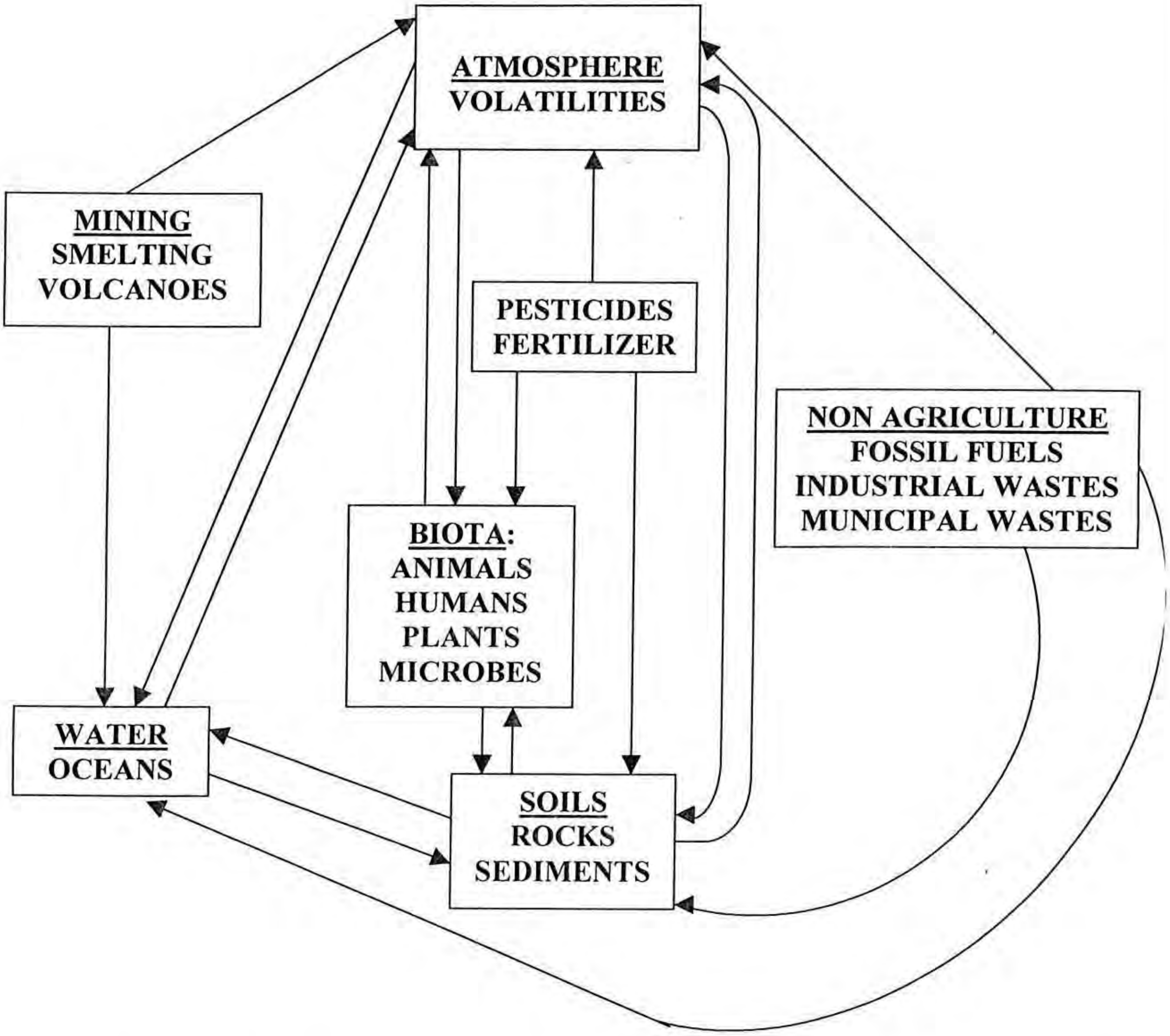


FIG. 2.1 Simplified Comprehensive Cyclic of Transfer of Arsenic (Bhumbla and Keefer, 1994)

2.1.3 MODERN USES OF ARSENIC

Elemental arsenic has few uses, one of which is to impart more nearly spherical shape in the manufacture of lead shot. It is also used in certain alloys to increase strength at elevated temperatures, in bronzing and in pyrotechniqes. All naturally occurring arsenic consists of the stable isotope arsenic –75; the radioactive isotopes arsenic –72, -74 and –76 have been used in medical diagnostic procedure. Arsenic oxides are used in pesticides and serves as a decolouriser in the manufacture of glasses and preservatives for hides. Arsenic pentoxides comprise a major ingredient of insecticides, herbicides and metal adhesive. Arsine (AsH_3) has been used as a doping agent for semiconductor and as a military poison gas. The arsenic sulphides are used as pigments and in pyrotechniqes. $NaH_2AsO_4.H_2O$ on heating forms a variety of condensed exo-anions, such as $Na_2H_2As_2O_7$, $Na_2H_2As_3O_{10}$ and ($NaAsO_3$). Some salts such as lead arsenate and calcium arsenate are useful for sterilizing soils and controlling pests, respectively. The dihydrogen arsenic itself is used in medicine, as are several other arsenic compounds. Most of the medical uses of arsenic compounds depend on their toxic nature. From 1860s until the introduction of DDT and other organic pesticides in the 1940s, inorganic compounds of arsenic remained the dominant insecticides available to farmers and fruit growers (Nriagu and Azcue, 1990).

The major use of arsenic, about 75% of the total consumption, still is in the agricultural field in the form of monosodium methylarstone (MSMA), di-sodium methylarsonate (DSMA), dimethylarsinic acid (Cacodylic acid) and arsenic acid (Nriagu and Azcue, 1994). Arsenic acid is used in the formation of wood preservative salts and sodium arsenate solutions are used for debarking trees in cattle and sheep dips and in aquatic weed control. Minor additions of arsenic (0.02-0.5%) to copper alloys raise the re –crystallization temperature and improve corrosion resistance (Carapella, 1978).

2.1.4 CHEMISTRY OF ARSENIC

2.1.4.1 CHEMICAL PROPERTIES

Arsenic is a chemical element in the nitrogen family (group VA of the periodic table), existing in both grey and yellow crystalline forms. It is widely distributed in nature and occasionally found un-combined, usually in association with such metals as antimony and silver. It also occurs combined in its sulphides realger and orpiment; as arsenic oxide and as a constituent of various metallic, sulphides of which arsenopyrite is the most abundant. Although some forms of arsenic are metal-like, it is best classified as non-metal (Encyclopaedia Britannica, 1994). There are three polymorphic modifications of arsenic. The cubic α form is made by condensing the vapour at very low temperatures, is metastable, is soluble in CS_2 and consists of tetrahedral As_4 units. The black β polymorph is isostructural with black phosphorus (II), also metastable and both of these modifications revert to the stable γ form, grey metallic, and rhombohedral arsenic on heating or exposure to light. Grey or metallic arsenic, which is more stable and more common than the softer yellow form, is very brittle, tarnishes in air and sublimes when heated strongly i.e. it passes directly into a vapour without melting and reverts to the crystalline solid without liquefying upon cooling the vapour (Encyclopaedia Britannica, 1994). The chemical properties are stated in Table 2.1.

2.1.4.2 PRINCIPAL COMPOUNDS OF ARSENIC

Because arsenic has a range of oxidation states from –3 to +5, it can form a variety of different kinds of compounds. Among the most important commercial compounds are the oxides, the principal forms of which are arsenious oxide (As_2O_3) and arsenic pentoxide (As_2O_5). Arsenious oxide, commonly known as white oxide, is the material most widely used for the synthesis of arsenic compounds. It is produced as a by-product of the nonferrous metal industry, primarily from the smelting of copper ores. Naturally occurring metal arsenides, realgar and orpiment also convert to the trivalent oxide when roasted in air. The formation of the trioxide by the roasting of a sulphide ore is illustrated below:

$$2FeAsS + 5O_2 \longrightarrow Fe_2O_3 + As_2O_3 + 2SO_2 \quad \text{..........................(I)}$$

$$4As + 3O_2 \longrightarrow 2As_2O_3 \quad \text{..(II)}$$

TABLE 2.1 Chemical Properties of Arsenic (Encyclopaedia Britannica, 1994)

Ser	Parameter	Value
1.	Atomic Number	33
2.	Atomic Weight	74.92158
3.	Melting point (grey form)	814^{0}C (1497^{0}F) at 36 atmosphere pressure
4.	Density (grey form) (yellow form)	5.73gm/cc at 14^0 C (57^{0}F), 2.03 gm/cc at 18^{0}C (64^{0}F)
5.	Boiling Point	616^{0}C (114^{0}F)
6.	Specific Gravity (α, β, γ)	2.0026, 4.7, 2.727
7.	Oxidation Number	-3,0, +3, +5
8.	Electronic Configuration	2-8-18-5$1s^22s^22p^63p^63d^{10}4s^24p^3$
9.	Electrical Resistivity	33.3 μ ohm cm (273k)
10.	Covalent Radius	121 pm
11.	Ionic Radius	69 pm
12.	Metallic Radius	139 pm
13.	Toxicity Level	0.5 mg.m^{-3} of air

The direct reaction between the elements yields the trioxide most conclusively. The reaction in air proceeds very slowly but the rate increases rapidly with increasing temperatures, decreasing particle size and the presence of moisture. The trioxide is moderately soluble in water, but dissolves easily in aqueous alkali to produce a solution of arsenic, AsO^{2-}. It is slightly soluble in polar organic solvents such as alcohols and ethers and insoluble in benzene. The most useful regent for the synthesis of pentoxides (As_2O_5) is concentrated nitric acid. The reaction between elemental arsenic and nitric acid gives the pentoxide.

$$4H_3AsO_4 \longrightarrow 6H_2O + As_4O_{10} \text{ ....(III)}$$

Hypochlorous, chloric and perchloric acids also oxidize the metal or As_2O_3, to the pentavalent state. Arsenic pentoxide dissolves readily in water to produce arsenic acid, H_3AsO_4. Arsine (AsH_3) is the best known of the hydrides of arsenic. It is a colourless poisonous gas composed of arsenic and hydrogen. The gas also called arsenic hydride, is produced by the hydrolysis and metal arsenides and by the reduction by metals of arsenic compounds in acidic polymeric diarsenic monohydride $(As_2H)_x$.

Arsenic pentoxide, the anhydride of arsenic acid, H_3AsO_4, is very soluble in cold water and dissolves to form a solution of arsenic acid. The free acid can be obtained as a hydrate, $H_3AsO_4.0.5H_2O$ by the evaporation of a cold aqueous solution. Arsenic acid is strong as H_3PO_4. Arsenic trioxide is the anhydride of arsenious acid. The rate of dissolution arsenic trioxide in water is painstakingly slow, sometimes requiring up to 50 hours of continuous agitation. The free acid has never been isolated. The solubility of arsenic trioxide increases greatly and occurs much more rapidly in both acid and alkaline media. Diarsenic disulphide, As_2S_2 exist in nature as mineral realgar. As_2S_2 is normally prepared as an impure material and must be purified by sublimation under an atmosphere of CO_2. Diarsenic trisulphide, As_2S_3 is found in nature as orpiment, has been referred to yellow arsenic sulphide. Diarsenic pentasulphide, As_2S_5, has been described a brownish-yellow, glassy, amorphous and highly refractive. When suspended in water and heated it decomposes into the thermodynamically more stable As_2S_3 and free sulphur. Two binary As-P compounds have been reported as As_2P and AsP. Diarsenic phophide is a black and lustrous and turning brown on exposure to air. AsP is described as a lustrous and red brown powder. Arsenic also forms numerous organic compounds like tetramethyldiarsine, $(CH_3)_2As\text{-}As(CH_3)_2$, used in preparing the common desiccant cacodylic acid. Several complex organic compounds of arsenic have been employed in the treatment of certain diseases, such as amebie dysentery caused by microorganism. Some of the most important compounds and species are shown in Table 2.2.

TABLE 2.2 Arsenic Compounds and Species and Their Environmental and Toxicological importance in Water (Source: Stuart et.al., 1996; Kartinen and Martin, 1995; WHO, 1996)

Compounds	**Example**	**Aquatic Environment**	**Toxicity**
Arsine	As^{3-}	Minor importance	Most toxic arsenic species
Elemental Arsenic	As	Minor importance	Least toxic arsenic species
Trivalent Arsenic	As(III)	Anaerobic	10 times more than As(V)
Arsenite	H_3AsO_3	pH=0-9	
Inorganic	$H_3AsO_3^-$	pH=10-12	
	$H_3AsO_3^{2-}$	pH=13	
	AsO_3^{3-}	pH=14	
MMAs(III)	$CH_3As(III)O_2^{2-}$	Several fungi and bacteria can methylate (As(III)	Less than inorganic As(III)
DMAs(III)	$CH_3As(III)O_2^-$		
TMAs(III)	$CH_3As(III)O_2$		
Organo-As(III)			
Pentavalent arsenic	As(V)	Aerobic	10 times less than As(III)
Arsenate	H_3AsO_4	pH=0-2	
Inorganic	$H_3AsO_4^-$	pH=3-6	
	$H_3AsO_4^{2-}$	pH=7-11	
	AsO_4^{3-}	pH=12-14	
MMAs(III)	$CH_3As(V)O_2^{2-}$	Methylation through reduction of As(V) to As(III)	Less than inorganic As(V)
DMAs(III)	$CH_3As(V)O_2^-$		
TMAs(III)	$CH_3As(V)O_2$	Minor importance	
Organo-As(III)			

2.1.4.3 AQUEOUS CHEMISTRY OF ARSENIC

Arsenic occurs in two forms: arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) ions, often referred to as arsenic (III) and arsenic (V) species due to the oxidation number of the central arsenic atom. The chemistry is complicated by the fact that each ion can acquire from water one or more protons, depending on the acidity, to yield a series of chemical species:

Arsenic(III) series	AsO_3^{3-}	$HAsO_3^{2-}$	$H_2AsO_3^-$	H_3AsO_3
Arsenic (V) series	AsO_4^{3-}	$HasO_4^{2-}$	$H_2AsO_4^-$	H_3AsO_4

At the acidity of drinking water, the dominant arsenic (III) species is the neutral compound $H_2AsO_4^-$. However, all arsenic(III) species coexist and rapidly interconvert, as is the case for arsenic (V) species. The arsenic(III) and arsenic(V) series can also interconvert. This is more difficult since oxidation or reduction processes are required, but conversion occurs slowly in rocks, groundwater and surface waters due to the influence of minerals, microorganisms and atmospheric oxygen. Arsenic(III) compounds are more toxic than arsenic (V) compounds, by a factor of about ten. The proportion of arsenic (III) in tubewell water typically ranges between 50 and 90%. Arsenic is a more strong acid than arsenious acid. within the range of natural waters, where pH is between 6 and 9, the trivalent inorganic arsenic is found as non-dissociated arsenious acid, while the pentavalent arsenic is primarily found as the ionised di-hydrogen arsenate and mono-hydrogen arsenate. The valence in which arsenic exists is related to both pH and the oxidation-reduction potentials, Eh. The hypothetical electron activity at equilibrium, pE, is used interchangeably with Eh. These parameters are simply related by $pE = (F/2.3RT)\,Eh$, where T is the absolute temperature and F and R are the Faraday and gas constants, respectively Thus at 25^0C, $2.3\ Rt/F = 0.058V\ mol^{-1}$ and $pE = Eh/0.059$ (Cherry, 1979).

The idea of using harmless metal ions, such as iron, copper, manganese or aluminium, to trap and remove arsenic species from drinking water as their insoluble salts is attractive since the chemicals required are inexpensive. Other metals with somewhat more soluble arsenic salts, such as magnesium and calcium, are also worthy of examination. Metal salts have been used for large-scale treatment of wastewaters for arsenic removal. However, the metal salts of arsenic(III) and arsenic(V) have widely different solubilities, and it is necessary to choose metals carefully. Arsenic(V) salts (metal arsenates) are generally less soluble than arsenic(III) salts (metal arsenites). It is vital, however, that arsenite(III) compounds be removed since they are the more dangerous (Crisp et.al,2001). Sparingly soluble metal arsenites and arsenates in equilibrium with water near neutral pH, generally yield concentrations of dissolved arsenic species greater than those acceptable in drinking water (50µg/L). On the other hand, binding of arsenic species to solid surfaces by adsorption may be extremely strong, since adsorption is frequently better for reducing the concentration of dissolved arsenic species than precipitation. Many ions in natural waters, particularly phosphate, may interfere with adsorption.

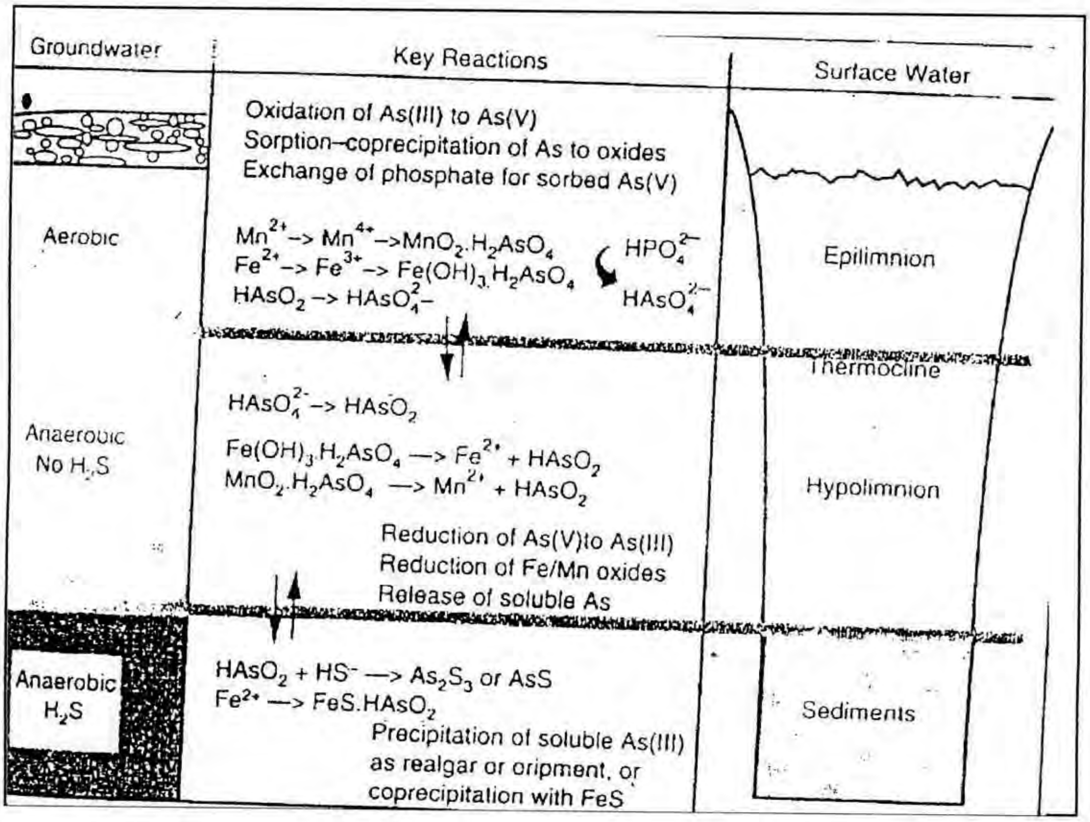


FIG 2.2 Arsenic Reactions in Aquatic Regime (Edward, 1994)

Sufficient excess adsorption capacity must be available or selective adsorbents used. Growth of algae in sections of the treatment system may be beneficial for removing phosphate ions. A cycle of arsenic in aquatic system is illustrated in Fig 2.2.

Calcium ions and hydrogen-carbonate ions are abundant in tubewell waters. When tubewell water is exposed to the air, carbon dioxide is lost and calcium carbonate precipitates. Iron (II) ions, also abundant in tubewell waters, are slowly oxidized by oxygen in the air, forming iron(III) hydroxide, which precipitates with the calcium carbonate. Large amounts of aqueous arsenic species are adsorbed by iron(III) hydroxide/calcium carbonate mixtures as they precipitate. Typically, half the arsenic(III) and nearly all the arsenic(V) species are removed.

2.1.5 GEOCHEMICAL PROCESS CONTROLLING ARSENIC MOBILITY

Two categories of processes largely control arsenic mobility in aquifers: (1) adsorption and desorption reactions and (2) solid-phase precipitation and dissolution reactions. Attachment of arsenic to an iron oxide surface is an example of an adsorption reaction. The reverse of this reaction, arsenic becoming detached from such a surface, is an example of desorption. Solid-phase precipitation is the formation of a solid phase from components present in aqueous solution. Precipitation of the mineral calcite, from calcium and carbonate present in ground water, is an example of solid-phase precipitation. Dissolution of volcanic glass within an aquifer is an example of solid-phase dissolution. Arsenic adsorption and desorption reactions are influenced by changes in pH, occurrence of redox (reduction/oxidation) reactions, presence of competing anions, and solid-phase structural changes at the atomic level. Solid-phase precipitation and dissolution reactions are controlled by solution chemistry, including pH, redox state, and chemical composition.

2.1.5.1 ADSORPTION AND DESORPTION PROCESSES

Arsenic is a redox-sensitive element. This means that arsenic may gain or lose electrons in redox reactions. As a result, arsenic may be present in a variety of redox states. Arsenate and arsenite are the two forms of arsenic commonly found in ground water. Arsenate generally predominates under oxidizing conditions. Arsenite predominates when conditions become sufficiently reducing. Under the pH conditions of most ground water, arsenate is present as the negatively charged oxyanions $H_2AsO_4^-$ or $HAsO_4^{2-}$, whereas arsenite is present as the uncharged species H_3AsO_3 (Hem, 1985). The strength of adsorption and desorption reactions between these different arsenic species and solid-phase surfaces in aquifers varies, in part, because of these differences in charge. Differences in species charge affect the character of electrostatic interactions between species and surfaces.

Arsenate and arsenite adsorb to surfaces of a variety of aquifer materials, including iron oxides, aluminium oxides, and clay minerals. Adsorption and desorption reactions between arsenate and iron-oxide surfaces are particularly important controlling reactions because iron oxides are widespread in the hydro geologic environment as coatings on other solids, and because arsenate adsorbs strongly to iron-oxide surfaces in acidic and near-neutral-pH water. However, desorption of arsenate from iron oxide surfaces becomes favoured as pH values become alkaline. The pH-dependence of arsenate adsorption to iron-oxide surfaces appears to be related to the change in iron-oxide net surface charge from positive to negative as pH increases above the zero-point-of about 7.7 for goethite (crystalline iron oxide or 8.0 for ferrihydrite (amorphous iron oxide). Where pH values are above 8, the negative net surface charge of iron oxide can repel negatively charged ions such as arsenate.

Iron-oxide surfaces also adsorb arsenite, and both arsenate and arsenite adsorb to aluminium oxides and clay-mineral surfaces. However, these adsorption reactions appear generally to be weaker than is the case for arsenate adsorption to iron-oxide surfaces under typical environmental pH conditions. Nevertheless, pH-dependent adsorption and desorption reactions other than those between arsenate and iron-oxide surfaces may be important controls over arsenic mobility in some settings. As is the case for adsorption of arsenate to iron-oxide surfaces, adsorption of arsenite to iron-oxide surfaces tends to decrease as pH increases, at least between the ranges from pH 6 to pH 9. Unfortunately, arsenate and arsenite adsorption and desorption reactions with other common surfaces are less tubewell characterized, and apparently more complex than is the case for adsorption and desorption reactions with iron-oxide surfaces. As a result of the pH dependence of arsenic adsorption, changes in ground-water pH can promote adsorption or desorption of arsenic. Because solid-phase diagenesis (water-rock interaction) typically consumes H+, the pH of ground water tends to increase with residence time, which, in turn, increases along ground-water flow paths. Because iron-oxide surfaces can hold large amounts of adsorbed arsenate, geochemical evolution of ground water to high (alkaline) pH can induce desorption of arsenic.

Similarly, redox reactions can control aqueous arsenic concentrations by their effects on arsenic speciation, and hence, arsenic adsorption and desorption. For example, reduction of arsenate to arsenite can promote arsenic mobility because arsenite is generally less strongly adsorbed than is arsenate. Redox reactions involving either aqueous or adsorbed arsenic can affect arsenic mobility. Arsenic adsorption also can be affected by the presence of competing ions. In particular, phosphate and arsenate have similar geochemical behaviour, and as such, both compete for sorption sites. Oxyanions in addition to phosphate also may compete for sorption sites.

Finally, structural changes in solid phases at the atomic level also affect arsenic adsorption and desorption. As ferrihydrite crystallizes into goe- thite, the density of arsenic adsorption sites decreases. This decrease in density of adsorption sites can result in desorption of adsorbed arsenic. Structural changes in other solid phases may possibly affect arsenic mobility, too. The role of such solid-phase structural changes on ground-water arsenic concentrations has, however, received little attention to date.

2.1.5.2 PRECIPITATION AND DISSOLUTION PROCESSES

The various solid phases (minerals, amorphous oxides, volcanic glass, organic carbon) of which aquifers are composed exist in a variety of thermodynamic states. At any given time, some aquifer solid phases will be undergoing dissolution, whereas others will be precipitating from solution. Arsenic contained within solid phases, either as a primary structural component of or an impurity in any of a variety of solid phases, is released to ground water when those solid phases dissolve. Similarly, arsenic is removed from ground water when solid phases containing arsenic precipitate from aqueous solution. As an example, because arsenic often co precipitates with iron oxide, iron oxide may act as an arsenic source (case of dissolution) or a sink (case of precipitation) for ground water. Furthermore, solid-phase dissolution will contribute not only arsenic contained within that phase, but also any arsenic adsorbed to the solid-phase surface. The process of release of adsorbed arsenic as a result of solid-phase dissolution is distinct from the process have desorption from stable solid phases.

2.1.6 BIOMETHYLATION OF ARSENIC

Endogenous thiols probably play a critical role in the metabolic conversion of As (III) and As (V) species. It is likely that glutathione (GSH) acts as a reducing agent for As(V) species; the resulting As(III) species can then accept a methyl group from S-adenosylmethionine (SAM) to produce the methyl-arsenic(V) species in an oxidative-addition reaction, as illustrated in Figure 2.3. This cycle of reaction followed by oxidative addition of methyl group can be continued and the end product seems to depend on the organism. The end products can be trimethylarsonnium ion for clams.

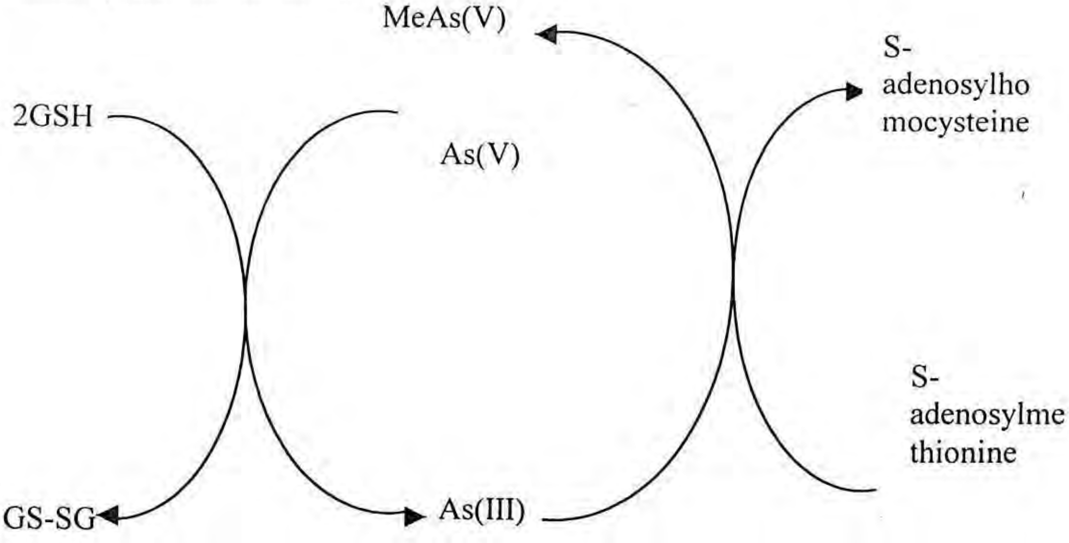


FIG. 2.3 Biomethylation of arsenic:SAM as methyl donor. GHS as reducing agent GSH, glutathione (Jemino and Nerigo, 1997)

SAM is probably the source of the adenosyl group that is found in the arsenosugars (Jemeno and Neriago, 1997). The As(III) derivatives seem to have the unique ability to accept all three groups that are attached to sulphur in SAM. The As(III) species that are intermediates in the biotransformation of arsenic might tubewell be toxic. For example, glutathione reductase mehylarsenic(III) and As(III) species. The action of GR is critical in maintaining the redox status of cells.

2.1.7 MECHANISM OF ARSENIC RELEASE IN GROUNDWATER

Among the natural sources, arsenopyrite (FeAsS) is the most common arsenic-bearing mineral (Ali and Ahmed, 2000). In addition many sulphide minerals, especially pyrite (FeS_2) is found to be rich in arsenic. Arsenic may leach into the groundwater as a result of oxidation of arsenopyrite and arsenic rich pyrite. Besides arsenic bearing minerals, arsenic is often present in sediments in association with iron oxyhydroxides. Arsenic derived from weathering of arsenic rich based metal sulphides may accumulate in iron oxyhydroxides because of its affinity for the latter. These arsenic rich iron hydroxides can be a major source of arsenic in groundwater. Thus in Bangladesh, two most probable natural sources responsible for arsenic contamination of groundwater are: (i) arsenopyrite (FeAsS) and arsenic rich pyrite, and (ii) arsenic rich iron oxyhydroxides.

2.1.7.1 ARSENOPYRITE AND ARSENIC RICH PYRITE

Oxidation of arsenic bearing sulphide minerals (such as FeAsS and FeS_2) in aquifer can release arsenic into groundwater. The rate oxidation of sulphide minerals is limited by the presence of an oxidizing agent, most commonly atmospheric oxygen (as O_2). Relatively deeper groundwater is isolated from atmosphere and the availability of oxygen in deep aquifers is limited by the amount of oxygen present in recharge water. Human activity that can significantly influence sulphide mineral oxidation and arsenic release into the aquifer is increased pumping of groundwater.

Increased pumping and reducing recharge can greatly accelerate oxidation rates of arsenic bearing sulphide minerals by lowering water table and exposing minerals to atmospheric oxygen. Oxidation of arsenopyrite (FeAsS) by oxygen and consequent release can be expressed by the following reactions:

$4FeAsS + 11O_2 + 6H_2O \rightarrow 4FeSO_4 + 4H_2AsO_3^- + 4H^+$.............(IV)

$4FeAsS + 13O_2 + 6H_2O \rightarrow 4FeSO_4 + 4H_2AsO_4^- + 4H^+$.............(V)

In the presence of oxygen, oxidation of pyrite mineral (FeS_2) may occur according to the following reactions:

$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4HSO_4^-$..(VI)

$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$..(VII)

$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$..............(VIII)

The Fe^{3+} ions formed act as a catalyst for further oxidation of pyrite. In absence of oxygen, nitrate can also act as an oxidising agent and can promote oxidation of arsenic bearing sulphide minerals. High nitrate concentrations from agricultural activities can therefore enhance arsenic release in groundwater.

2.1.7.2 ARSENIC RICH IRON HYDROXIDE

Arsenic derived from weathering of arsenic rich base metal sulphides are often found to be associated with iron oxyhydroxides in downstream sediments. Arsenic has high affinity for hydrous iron oxyhydroxides and becomes associated with them as a result of adsorption. Sediments in the Ganges delta region are known to have iron oxyhydroxides coatings on the mineral grains and at many places these coatings have been found to be rich in arsenic. Arsenic can be released from arsenic iron oxyhroxides as a result of dissolution and desorption. Dissolution of oxyhydroxides can be caused by reducing redox environment in the subsurface. Organic matter, which is present in abundance in alluvial sediments, can be responsible for reducing environment. Reducing redox release of associated arsenic into groundwater. In addition, lowering of pH can also promote dissolution of iron from oxyhydroxides and subsequent release of associated arsenic as shown below:

$Fe(OH)_{3(s)} + e^- \rightarrow Fe^{2+} + 3OH^-$ ....(IX)

$Fe(OH)_{3(s)}.AsO_4^- \rightarrow Fe(OH)_2^+As + H_2O$ ....(X)

At high pH values exceeding 8, adsorption of arsenic on oxide surface decreases and desorption of arsenic from iron hydroxide surface can be promoted by an increase of pH. However, such high pH values are not common for groundwater in Bangladesh and this mechanism does not appear to play a major role in the release of arsenic in the subsurface. Possible adsorption desorption reactions of arsenate on hydroxide surface are shown below:

$Fe(OH)^0 + AsO_4^{3-} + 3H^+ = FeH_2AsO_4 + H_2O$ ....(XI)

$Fe(OH)^0 + AsO_4^{3-} + 2H^+ = FeHAsO_4^- + H_2O$ ....(XII)

Desorption of arsenic from iron hydroxides can be promoted in the presence of a competing anion such as phosphate (PO_4^{3-}). Possible reaction for such desorption are shown below:

$FeH_2AsO_4 + PO_4^{3-} = FeH_2PO_4 + AsO_4^{3-}$ ....(XIII)

$FeHAsO_4^- + PO_4^{3-} = FeHPO_4^- + AsO_4^{3-}$ ....(XIV)

Thus application of phosphate fertilizer can potentially increase arsenic concentration in groundwater as a result of replacement of arsenic by phosphate ions on adsorption sites of iron oxyhydroxides.

2.1.8 ARSENIC MOBILIZATION IN SOIL WATER ENVIRONMENT

Arsenic occurs in soils at an average concentration of about 5 to 6 mg/l, but mean arsenic contents in soil is as high as 20 ppm in Italy, 14 ppm in Mexico, 11.2 ppm in China and 11 ppm in Japan have been reported (Yan-Chu, 1994). The presence of high concentration of arsenic in groundwater is not generally dependent on the concentration of arsenic in soils. The solubility of arsenic in water is usually controlled by redox conditions, pH, biological activity and adsorption reactions. The reducing condition at low Eh value converts arsenic into a more mobile As(III) form, whereas at high Eh value, As(V) is the major arsenic species (Ahmed, 2000). Arsenic in soils is relatively stable at neutral pH and exhibits mobility both at higher and lower pH values. At lower pH levels, metal ions solubilize from the sediments with concurrent release of arsenic species. At high pH levels, the increased hydroxide concentrations cause displacement of arsenic species from their binding sites. Desorption of arsenic can also be promoted in the presence of more competing anions such as phosphate.

Oxidation of soils may be caused by aeration due to seasonal water level fluctuations or water table lowering by large-scale withdrawal of groundwater. Soils may also be oxidized by infiltration of water saturated with dissolved oxygen. Chemical forms and transformation of arsenic in soils are illustrated in Fig 2.4. Arsenic can be mobilized from soil in a reducing environment. The reduction process converts precipitated and adsorbed As(V) into more soluble As(III):

$$H_2AsO_4^- + 3H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O \text{ ....(XV)}$$

In the reducing soil environment, arsenic will dominate in pore water as As(III). Further reduction of As(III) in the presence of sulphides will immobilize arsenic in soils with the formation of arsenic sulphide precipitates:

$$2H_3AsO_3 + 6H^+ + 3S^{2-} \rightarrow As_2S_3 + 6H_2O \text{ .... (XVI)}$$

$$2As_2S_3 + 4e^- \rightarrow 4AsS + 2S^{2-} \text{ ....(XVII)}$$

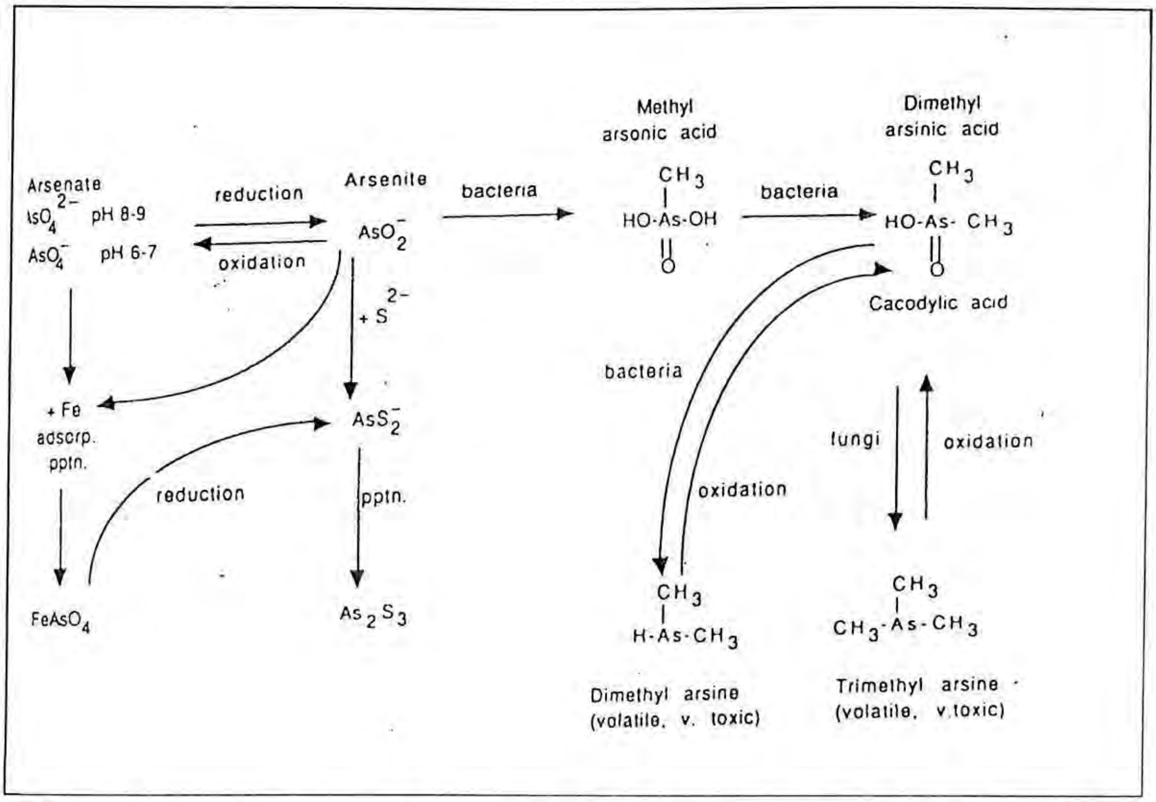


FIG. 2.4 Chemical Forms of Arsenic and their Transformation in Soils (Bhumbla and Keefer, 1994)

2.1.9 TECHNOLOGIES FOR ARSENIC REMOVAL

2.1.9.1 INTRODUCTION

Most of the established technologies for arsenic removal make use of processes like Oxidation/reduction, Precipitation, Adsorption, Solid/liquid separation, Physical exclusion, Biological removal processes etc, either at the same time or in sequence. All of the technologies have the added benefit of removing other undesirable compounds along with arsenic depending on the technology; bacteria, turbidity, colour, odour, hardness, phosphate, fluoride, nitrate, iron, manganese and other metals can be removed. Historically, the most common technologies for arsenic removal have been coagulation with metal salts, lime softening and iron/manganese removal. Since the WHO Guideline value for arsenic in drinking was lowered from 50 to 10μg/L in 1993, several countries have lowered their drinking water standards in some cases to 10μg/L (Johnston and Heijnen, 2001).

Coagulation processes are sometimes unable to efficiently remove arsenic to these low levels. As a result, various alternate technologies have been developed or adapted that are capable of removing arsenic to trace levels. These advanced treatment options include ion exchange, activated alumina and membrane methods such as reverse osmosis and nanofiltration. While these technologies have all been shown to be effective in lab or pilot studies, there is still relatively little experience with full-scale treatment. The main arsenic removal technologies are presented below, along with a brief description of how removal efficiency is affected by arsenic concentration and speciation, pH, and the presence of other dissolved constituents.

2.1.9.2 OXIDATION

Most arsenic removal technologies are most effective at removing the pentavalent form of arsenic (arsenate), since the trivalent form (arsenite) is predominantly non-charged below pH 9.2. Therefore, many treatment systems include an oxidation step to convert arsenite to arsenate. Oxidation alone does not remove arsenic from solution and must be coupled with a removal process such as coagulation, adsorption or ion exchange. Arsenite can be directly oxidised by a number of other chemicals, including gaseous chlorine, hypochlorite, ozone, permanganate, hydrogen peroxide and Fenton's reagent (H_2O/Fe^{2+}). Some solids such as manganese oxides can also oxidise arsenic. Ultraviolet radiation can catalyse the oxidation of arsenite in the presence of other oxidants, such as oxygen. Direct UV oxidation of arsenite is slow, but may be catalysed by the presence of sulphide (Ghurye and Clifford, 2000), ferric iron (Emett and Khoe, 2001) or citrate (EAWAG, 1999). Chlorine is a rapid and effective oxidant, but may lead to reactions with organic matter, producing toxic trihalometanes as a by-product.

In Europe, and increasingly in the USA, ozone is being used as an oxidant. In developing countries, ozone has not been widely used. An ozone dose of 2mg/L, contacted with the water for 1 minute prior to filtration, has been shown to be effective in oxidising iron and manganese, at the same time removing arsenic and other metals to below detection limits (Nieminski and Evans, 1995). Ozone is also a potent disinfectant, but unlike chlorine, does not impart a lasting residual to treated water. Permanganate effectively oxidises arsenite, along with Fe(II) and Mn (II). It is a poor disinfectant, though it can produce a bacteriostatic effect. Hydrogen peroxide may be an effective oxidant if the aw water contains high levels of dissolved iron, which often occur in conjunction with arsenic contamination.

2.1.9.3 COAGULATION AND FILTRATION

The most heavily documented treatment methods for arsenic removal involve coagulation and filtration, either using metal salts or lime softening. This treatment can effectively remove many suspended and dissolved constituents from water besides arsenic, notably turbidity, iron, manganese, phosphate and fluoride. Significant reductions are also possible in odour, colour, and potential for trihalomethane formation. Thus coagulation and filtration to remove arsenic will improve other water quality parameters, resulting in ancillary health and aesthetic benefits. However, the optimal conditions vary for removal of different constituents, and coagulation to remove arsenic may not be optimal for removal of other compounds, notably phosphate and fluoride.

Arsenic removal with metal salts has been shown since at least 1934 (Buswell, 1943). The most common used metal salts are aluminium salts such as alum and ferric salts such as ferric chloride or ferric sulphate. Excellent arsenic removal is possible with either ferric or aluminium salts, with laboratories reporting over 99% removal under optimal conditions. During coagulation and filtration, arsenic is removed through three main mechanisms (Edwards, 1994):

- Precipitation: The formation of t he insoluble compounds Al (AsO_4) or $Fe(AsO_4)$.
- Coprecipitation: The incorporation of soluble arsenic species into a growing metal hydroxide.

- Adsorption: The electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxide.

All three of these mechanisms can independently contribute towards contaminant removal. In the case of arsenic removal, direct precipitation has not been shown to play an important role. However, coprecipitation and adsorption are both active arsenic removal mechanisms. Numerous studies have shown that filtration is an important step to ensure efficient arsenic removal. Coagulation and sedimentation without filtration achieve arsenate removal efficiencies of 30%; after filtration through a 1.0-micron filter, efficiency is improved to over 96% (Hering et al., 1996).

2.1.9.4 ION EXCHANGE RESINS

Synthetic ion exchange resins are widely used in water treatment to remove many undesirable dissolved solids, most commonly hardness, from water. These resins are based on a cross-linked polymer skeleton, called the 'matrix'. Most commonly, this matrix is composed of polystyrene cross-linked with divinylbenzene. Charged functional groups are attacked to the matrix through covalent bonding and fall into four groups (Clifford, 1999):

- Strongly acidic (e.g. sulphonate, $-SO_3^-$)
- Weakly acidic (e.g. carboxylate, $-COO^-$)
- Strongly basic [e.g. quaternary amine, $-N^+(CH_3)_3$]
- Weakly basic [e.g. tertiary amine, $-N(CH_3)_2$]

The acidic resins are negatively charged and can be loaded with cations (e.g. Na^+), which are easily displaced by other cations during water treatment. This type of cation exchange is most commonly applied to soften hard waters. Conversely, strongly basic resins can be pre-treated with anions, such as Cl^- and used to remove a wide range of negatively charged species. Clifford gives the following relative affinities of some common anions for a type 1 strong-base anion resins (Clifford, 1999).

$CrO_4^- > SeO_4^{2-} > SO_4^{2-} > HSO_4^- > NO_3^- > Br^- > HAsO_4^{2-} > SeO_3^{2-} > HSO_3^{3-} >$
$NO_2^- > Cl^-$

Conventional sulphate-selective resins are particularly suited for arsenate removal. Conventional sulphate selective resins are particularly suited for arsenate removal. Nitrate selective resins also remove arsenic, but arsenic breakthrough occurs earlier. Most commonly, resins are pre-treated with hydrochloric acid, to establish chloride ions at the surface, which are easily displaced by arsenic (Ghurye et al., 1999), though the resin can be primed with other anions such as bromide or acetate (Edward et al., 1998). Arsenate removal is relatively independent of pH and influent concentration. On the other hand, competing anions, especially sulphate, have a strong effect. In low sulphate waters, ion exchange resin can easily remove over 95% of arsenate, and treat from several hundreds to over a thousand bed volumes before arsenic breakthrough occurs.

2.1.9.5 ACTIVATED ALUMINA

Activated alumina is a granulated form of aluminium oxide (Al_2O_3) with very high internal surface area, in the range of 2000-300 m^2/g. This high surface area gives the material a very large number of sites where sorption can occur and activated alumina has been widely used for removal of fluoride. The mechanism of arsenic removal are similar to those of a weak base ion exchange resin and are often collectively referred to as 'adsorption', though ligand exchange and chemisorptions are technically more appropriate terms (Clifford, 1999). The kinetics of arsenic removal onto the alumina surface is slower than those of ion exchange resins and some arsenic leakage is often noted in activated alumina systems.

Arsenic removal efficiency is excellent (typically> 95%), for both arsenite and arsenate, but arsenic capacity varies significantly and is controlled primarily by a pH and influent arsenic concentration and specification. Arsenate removal capacity is best in the narrow range from pH 5.5 to 6.0, where the alumina surfaces are promoted, but acid anions are not yet concentrated enough to compete with arsenic for sorption sites (Trussel et al., 1980). Typically, activated alumina has a point of zero charge (PZC), below which the surface is positively charged and above which the surface bears a negative charge, at pH 8.2. Arsenic removal capacity drops sharply as the PZC is approached and above the pH 8.5, is reduced to only 2-5% of capacity at optimal pH (Clifford, 1999). Fro neutral and basic waters, therefore, pH adjustment may be necessary for effective arsenic removal. Fine particles of activated alumina are typically used for arsenic removal, with an empty bed contact time of five to eight minutes (Rubel and Woosely, 1979). When operated in the optimal pH range, activated alumina beds have much longer run times than ion exchange resins. The number of bed volumes that can be treated at optimal pH before arsenate breaks through is mainly controlled by the influent arsenic concentration. Frank and Clifford reported an arsenate capacity (at pH 6) of about 1.6 g/L of activated alumina, consistent with an earlier reported capacity of 4 mg/g, assuming a bulk density of 0.5 kg/L (Gupta and Chen, 1978). Activated alumina can be regenerated by flushing with a s solution of 4% sodium hydroxide, which displaces arsenic from the alumina surface, followed by flushing with acid, to re-establish a positive charge on the grain surfaces. Regeneration is more difficult and less complete (generally 50-80%) than with ion exchange resins (Clifford, 1986). The advantages of activated alumina are that simple removal systems can be developed at community or household levels that require no chemical addition.

2.1.9.6 MEMBRANE METHOD

Synthetic membranes are available which are selectively permeable: the structure of the membrane is such that some molecules can pass through, while others re excluded, or rejected. Membrane filtration has the advantage of removing many contaminants from water, including bacteria, salts and various heavy metals. Two classes of membrane filtration can be considered: low-pressure membranes, such as microfiltration and ultrafiltration; and high–pressure membranes such as nanofiltration and reverse osmosis. Low-pressure membranes have larger nominal pore sizes and are operated at pressures of 10-30 psi. The tighter high–pressure membranes are typically operated at pressures from 75 to 250 psi, or even higher (Letterman, 1999). Arsenic removal was found to be independent of pH and the presence of co-occurring solutes, but somewhat improved at lowered temperatures. Membrane filtration requires a relatively high-quality influent water, particularly organic matter. Iron and manganese can also lead to scaling and membrane fouling. To prevent fouling, reverse osmosis filters are almost always preceded by a filtration step.

Membrane filtration has the advantage of lowering the concentrations of many other components in addition to arsenic. Even ultrafiltration (UF) membranes are able to remove over 99.9% of bacteria, Giardia and viruses. Also, the membrane itself does not accumulate arsenic, so disposal of used membranes would be simple. Operation and maintenance requirements are minimal: no chemicals need be added and maintenance would consist of ensuring a reasonably constant pressure and periodically wiping the membrane clean. The main advantages are low water recovery rates (typically only 10-20% of the raw water passes through membrane), the need to operate at high pressures, relatively high capital and operating costs and the risk of membrane fouling. Also particularly with reverse osmosis, the treated water has very low levels of dissolved solids and can be very corrosive and deficient in minerals which can be important micronutrients for humans.

2.2 IRON

2.2.1 INTRODUCTION

Iron is a highly objectionable constituent in water supplies for either domestic or industrial use. According to the World Health Organisation (WHO,1996) International Standards for Drinking Water, the maximum permissible concentration of iron in potable water is 0.3 mg/l. This limit is based on aesthetic, taste and nuisance considerations. Industry on the other hand may have more demanding requirements as to the critical concentration of iron in their process or cooling water. Iron exists in chemically reduced soluble form in ground water. In presence of oxygen soluble iron oxidises to insoluble form, which then precipitated out. The chemistry of iron in natural water system involves a number of factors ranging from he E_h to the impact of organic complexing agent. The highly complex nature of water chemistry of this species serves to complicate the literature on iron chemistry. As a result, the typical phenomenological approach utilized in the water treatment studies, wherein chemicals are added and percent removals are observed frequently does more to confuse the state of the art than to advance it. A number of factors such as pH, which has been indicated by Stumm and Lee (1961) to increase the rate of ferrous iron oxidation by 100-fold per pH unit, bicarbonate, sulphate and dissolved silica which were indicated by Schenk and Webber (1968), have significant impacts on the rate of oxidation. Further complicating the reaction system for iron is the impact of organic complexing agent. Various humics and similar materials can act to complex the iron and to slow down the kinetics of the oxidation.

2.2.2 OCCURRENCE OF IRON

The element iron is an abundant and widespread constituent of rocks and soils. Dissolved iron is found is ground water from tubewells located in shale, sandstone and alluvial deposits. In igneous rocks the principal minerals containing iron as an essential component include the pyroxenes, amphiboles, magnetite and the nesosilicates such as olivine. The composition of olivine ranges from Mg_2 SiO_4 to Fe_2 SiO_4 with ferrous iron substituting freely for magnesium. Most commonly, the iron in igneous rocks is in the ferrous form, but may be mixed with ferric iron as in magnetite (Fe_3O_4) (Hem. 1970). Common minerals (deposits) of iron include ferric oxide and hydroxides such as hematite (Fe_2O_3) and ferric hydroxide [$Fe(OH)_3$]. Sedimentary forms of iron include sulphides, such as pyrite and marcasite; two minerals with identical chemical composition (FeS_2) but different crystalline structures; carbonates such as siderite ($FeCO_3$); and mixed oxides such as magnetite (Fe_3O_4). The ferrous oxides and sulphides are the usual sources of dissolved iron in ground water. Weathering of iron silicates can produce dissolved iron in near surface water; however, this is a relatively slow process.

Ferrous iron (Fe^{2+}) is chemically reduced, soluble from that exist in a reducing environment (absence of dissolved oxygen and low pH). Many ground waters are low in dissolved oxygen and are supersaturated with carbon-di-oxide, owing to weathering of carbonate rocks or the increased carbon-di-oxide concentration in the soil gas. The lower pH value of ground water due to the presence of carbon -di-oxide and mineral acids and absence of dissolved oxygen creates favourable conditions to hold iron in high concentration in ground water as ferrous bicarbonate (Bell, 1965).

$$Fe^{2+} + 2\,CO2 + 2H2O \xrightarrow{\qquad} Fe(HCO_3)_2 + 2H^+ \text{.............(XVIII)}$$

Upon exposure to the atmosphere dissolution of carbon-di-oxide from supersaturated groundwater occurs, leading to an increase in pH value. At the same time aeration of the ground water occurs and increases the dissolved oxygen concentration. As a result rate of oxidation of soluble ferrous iron to insoluble ferric iron increases, which precipitates from solution as hydrous ferric oxides.

$$2Fe^{2+} + 4HCO_3^{\,-} + H2\,O + {}^1/_2\,O_2 \xrightarrow{\qquad} 2Fe\,(OH)_3 + 4CO_2 \text{......(IXX)}$$

The oxidation of iron in nature system is more complex than indicated by the above equation.

Iron can also enter in water through solution or infusion of organic bodies such as wood leaves and so forth. Iron is an essential element in both plant and animal metabolism. Iron, therefore, is to be expected in organic wastes and in plant debris in soil and the activities in the biosphere may have a strong influence on the occurrence of iron in water (Hem, 1970). Iron may be present as soluble ferrous bicarbonate in alkaline tubewell or spring waters; as soluble ferrous sulphate in acid drainage waters or waters containing sulphur; as soluble organic carbon in coloured swamp waters; as suspended in soluble ferric hydroxide formed from iron bearing will waters, which are subsequently exposed to air; and as a product of pipe corrosion producing red water (Ali, 1990).

2.2.3 IRON PROBLEM AREAS OF BANGLADESH

Ground water collected through hand pump tube tubewells in Bangladesh carries a high concentration of iron and in many locations the concentration is much higher than the acceptable limit. This is probably because of the fact that alluvial deposits containing trace of iron compounds underlie most of the places of Bangladesh and shallow hand pump tube tubewells are drilled in such deposits to collect water.

A study by Ahmed, et.al.(1989) about the ground water quality of shallow aquifers reveals that iron content of ground water in most of the places of Bangladesh is greater than 1.00mg/L and in many locations the iron content of ground water is more than 5 mg/L. The study also shows that ground water of about 65% of the area of Bangladesh has average iron content more than 2 mg/l. A recent study on occurrence of iron in deep tube tubewell ground water has been performed by Hossain and Huda (1997). In that study it has been pointed out that 19.5% area of Bangladesh contain iron more than 5 mg/L and 64.5% of the total contains iron less than 1 mg/L. Iron concentration in deep tube tubewell water in Bangladesh exceeding 1.0 mg/L and exceeding 5.0 mg/L are shown in Figure: 2.5 and Figure: 2.6 respectively (Huda, 1995). The World Health Organisation (1983) suggested a guideline value of 0.3 mg/L of iron for drinking water. This limit can hardly be maintained in rural water supply in Bangladesh. For this reason, the Department of Environment (DOE, 1991), Bangladesh, recommended a desirable limit of 1 mg/l of iron in drinking water. But in the case of hand pump tube tubewells in rural areas, the maximum tolerable limit was set at 5 mg/L in the absence of a better source. This local standard is being followed in rural water supply in Bangladesh. Based on the distribution of iron bearing aquifers, allowable limits in Bangladesh and people's acceptability, the country may be divided into three iron problem areas (Ali, 1990).

2.2.4 CHEMISTRY OF IRON CONTENT WATER

Iron (II) (Fe^{2+}) is a chemically reduced, soluble form that may exist in a reducing environment. Upon exposure to the atmosphere dissolution of carbon-di-oxide and H_2S from supersaturated ground water occurs, leading to an increase in pH value. At the same time aeration of the ground water occurs and increases the dissolved oxygen concentration. Thus aeration and dissolution of carbon-di-oxide increases the rate of oxidation of soluble ferrous iron to insoluble ferric iron. But the oxidized and precipitated iron particles are so small in size that is very difficult to separate them through sedimentation. Coagulation and flocculation are the process by which these small particles are allowed to grow or flocculate to sizes that settle at satisfactory velocities.

2.2.5 SOLUBILITY OF IRON

In the pH range encountered in natural waters, soluble ferrous iron consists primarily of Fe^{2+} and $FeOH^+$. While greatly limited in solubility at neutral pH, the aqueous ferric ions consist predominantly of $Fe\ (OH)^{2+}$ and $Fe\ (OH)_4$ (O Connor, 1971). According to Ghosh, et al. (1966) In alkaline natural water, the solubility of ferrous iron is limited by the solubility of ferrous carbonate in the pH range of 6-9, above which the solubility equilibrium of ferrous hydroxide becomes limiting again. Theoretically, iron that precipitates from a supersaturated solution of this type would be either ferrous carbonate of ferrous hydroxide depending on the pH. Under practical conditions, however the precipitation of basic carbonates, e.g. $[Fe\ (OH)_2 . FeCO_3]$ with somewhat different solubility characteristics is probable, especially in the pH range of 8 to 11. On aeration or by the addition of oxidizing agents, iron is oxidized from the ferrous to ferric form. Once oxidized, the solubility of iron is severely limited over a wide range of pH values from 4 to 13 by the solubility of ferric hydroxide. Complex formation of ferric ions with o-phosphate silicate and many organic bases is stable and very difficult to precipitate.

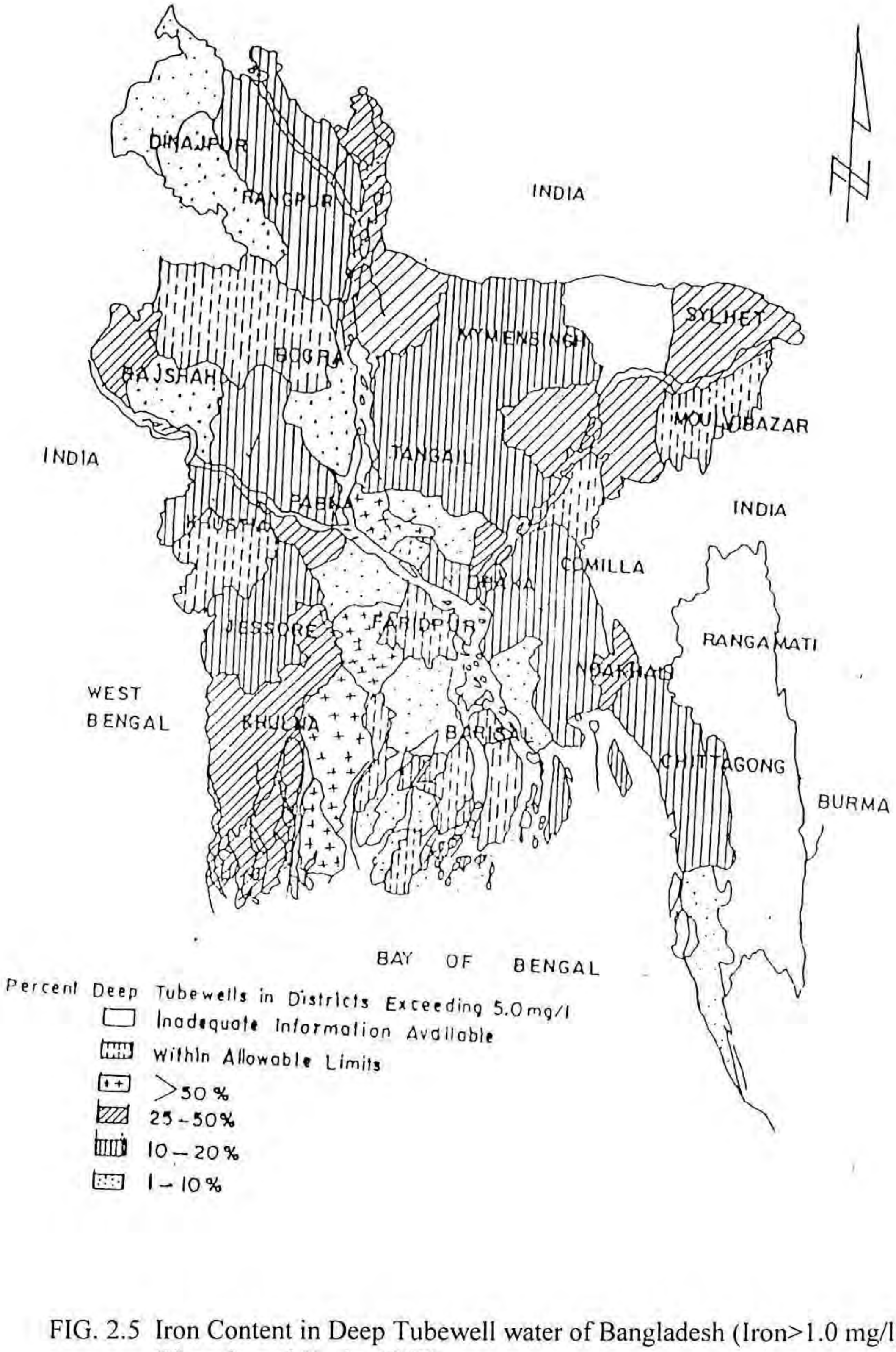


FIG. 2.5 Iron Content in Deep Tubewell water of Bangladesh (Iron>1.0 mg/l) (Hossain and Huda, 1997)

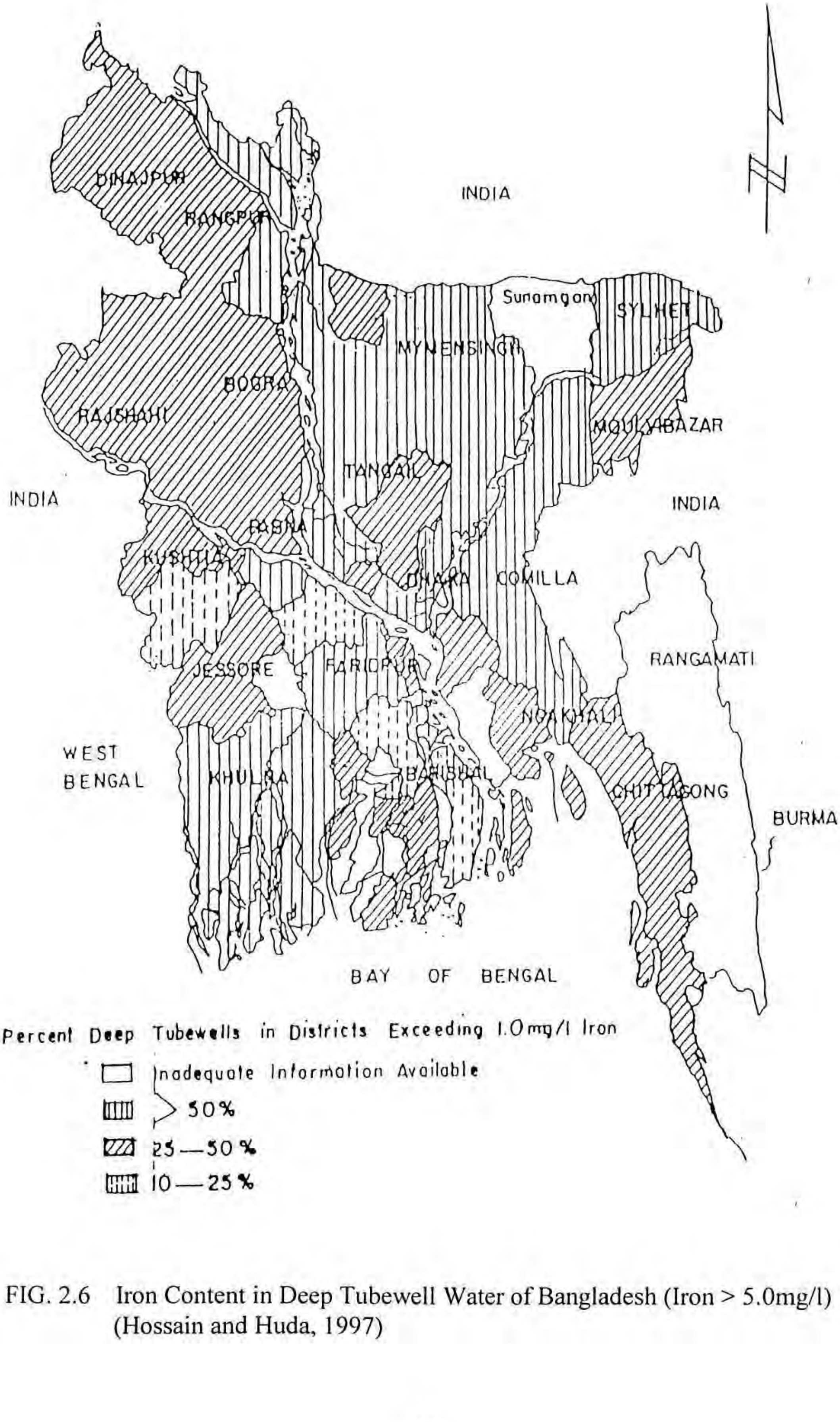


FIG. 2.6 Iron Content in Deep Tubewell Water of Bangladesh (Iron > 5.0mg/l) (Hossain and Huda, 1997)

2.2.6 KINETICS OF IRON OXIDATION

In the presence of dissolved oxygen, soluble ferrous iron (Fe^{2+}) oxidizes to ferric oxides or hydroxides. The stoichiometric relationship being (O Connor, 1971)

$$Fe^{2+} + {}^{1}/_{4}\, O_2 + 2OH^- + {}^{1}/_{2}\, H_2O \longrightarrow 2Fe(OH)_{3(s)} \text{ ....(XX)}$$

Which indicates that 1mg/l of oxygen will oxidize 7 mg/l of ferrous iron. So the oxygen demand and correspondingly the oxygen gas transfer requirements are very small. It is believed that the oxidation of ferrous iron proceeds stepwise through various ferrous-ferric species.

2.2.6.1 EFFECT OF Fe^{2+} AND pO_2

Gosh et all (1966) stated that rate of ferrous iron oxidation is of the first order with respect to ferrous iron concentration, Fe^{2+} and the partial pressure of oxygen, pO_2

Thus the rate law constant

$$-d/dt\,[Fe^{2+}] = K1\,[Fe^{2+}]pO_2 \text{ ....(XXI)}$$

It was also observed that the rate of iron oxidation remains unaffected by dissolved oxygen if the concentration exceeds 5 mg/l.

2.2.6.2 EFFECT OF pH VALUE

Usually ground water contains a high concentration of CO_2. The addition of O_2 to water not only results in the oxidation of ferrous iron but also serves to remove CO_2 resulting in an increase in pH. Oxidation of ferrous iron increases rapidly at pH of 7.0 or above and is very show below 6.0. Reaction rates are strongly pH dependent. Stumm and Lee (1961) indicated that an increase of one pH unit causes 100 fold increase in the rate of reaction i.e. there is a second order relationship between the rate of reaction and the hydroxyl ion concentration.

Therefore,

$-d/dt\ [Fe^{2+}]=K\ [Fe^{2+}]\ pO_2\ [OH^-]^2$ ....(XXII)

Where

$d[Fe\ (II)]/dt$ = Rate of iron (II) oxidation, mol / (l) (min)
Fe(II) = Ferrous ion concentration, mol/l
pO_2 = Partial pressure of oxygen, atmosphere
OH = Hydroxide ion concentration, mol/l
K = Reaction rate constant = 8.0 (±2.5) x 10^{13} xL^2/(min) (atm)$(mol)^2$ at 20.5^0 C

It has been observed that, the half time for Fe^{2+} oxidation at pH 7.02 is approximately 4 minutes and at pH 7.24 it is around 2 minutes, implying complete (>99%) oxidation of Fe^{2+} in a relatively short time in tubewell aerated water at pH values greater than 7.2 and alkalinity above 450 mg/L as $CaCO_3$ (Stumm and Lee 1961).

2.2.6.3 EFFECT OF ALKALINITY

Stumm and Lee reported that the reaction rates obtained in solutions of lower alkalinities tend to be of smaller magnitude and more scattered than those obtained in solutions of higher alkalinities. Robinson and Dixon (1968) mentioned that in order obtain complete oxidation of the ferrous iron; the bicarbonate alkalinity of the water should be in excess of 100mg/l as $CaCO_3$. Generally, if the concentration of alkalinity reaches 130 mg/l as $CaCO_3$ all of the ferrous iron will be oxidized almost immediately and any further addition of chemicals would appear to be unnecessary. Low alkaline water needs some oxidizing agent ($KMnO_4$) without raising pH and alkalinity or some chemical additive ($Na_2\ CO_3$) to raise both pH and alkalinity.

2.2.6.4 EFFECT OF TEMPERATURE

The reaction rate is dependent on temperature. For a given pH value, the rate increases about 10 fold for a 15^0 C increase in temperature, which is mainly caused by the change in $(OH)^-$ concentration due to temperature dependence of the ionisation constant of water (Stumm et.al.1961)

2.2.6.5 EFFECT OF IONIC STRENGTH

Sung and Forbes (1984) showed that the rate constant K is also a function of ionic strength and the presence of complex forming anions. They observed a linear variation of the rate constant up to an ionic strength 0.25 M in their study. At values greater than this, increasing ionic strength actually increases the rate constant.

2.2.6.6 EFFECT OF CHLORIDE AND SULPHATE

Sung and Morgan (1980) observed that chloride and sulphate ions have a significant retarding influence on the rate constant in the pH range from 6.5 to 7.2. Later sung and Forbes (1984) mentioned that for typical water iron removal, chloro-complexes of iron could probably be ignored because the effect of ionic strength and chloro-complexation may not be as important as the effects of temperature and pH.

2.2.6.7 EFFECT OF ORGANIC MATTER

Ferrous iron is capable of forming complexes with organic matter and as such, is resistant to oxidation even in the presence of dissolved oxygen. The relative strength of such complexes has a stability constant of approximately 10^4 (Theis and Singer, 1974).

2.2.6.8 CATALYTIC EFFECT

For a given pH value and oxygen concentration the addition of as little as 0.02 mg/l of Cu^{2+}, reduces the oxygenation time by a factor of 5 (Stumm and Lee, 1961). Sung and Morgan (1980) studied the effect of ferric hydroxide on the oxygenation of ferrous iron and stated that auto Catalysis is noticeable only for pH around 7 and above. Cox (1969) has described the use of contact bed oxidation in iron removal. The purpose of contact bed according to him is to facilitate oxidation of iron of manganese through the catalytic action of previously precipitated oxides of these minerals on the gravel or ore.

2.2.6.9 RATE OF IRON PRECIPITATION

When alkaline groundwater supersaturated with respect of ferrous carbonate is aerated, the pH increases because of the loss of carbon di oxide, thereby further increasing the degree of super saturation. As a result the precipitate formed may be expected to contain both ferrous carbonate and ferric hydroxide. The rate of precipitation of iron would therefore be determined by the rate of oxidation of ferrous iron plus the rate of ferrous carbonate precipitation (Ghosh et.al.1966) (see Fig. 2.7).

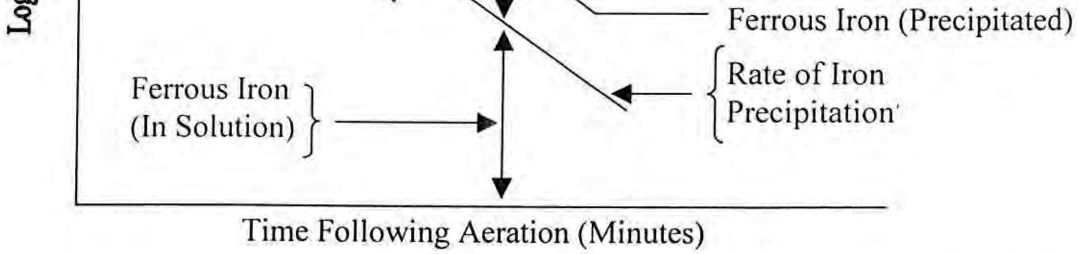


FIG. 2.7 Rate of Iron Oxidation and Rate of Iron Precipitation (Ghosh et. al., 1966)

In water having low alkalinities and, hence low buffer capacities, the pH will decrease gradually as the iron hydrolyses resulting in an increase in acidity of the waters (Ghosh et.al. 1966) In such cases it has been suggested to use soda ash, lime or caustic soda to raise the bicarbonate alkalinities to 100-130 mg/L as $CaCO3$. Potassium permanganate can be used as an oxidant to oxidize ferrous iron in natural water without raising the pH or the alkalinity.

2.2.7 TECHNOLOGIES FOR IRON REMOVAL

2.2.7.1 GENERAL

To remove soluble iron it is generally accepted that an oxidation process followed by a suspended solids removal process is most effective. Usually oxidation of soluble iron is accomplished by simple aeration or chlorination/potassium permanganate application. Coagulation/flocculation with sedimentation and filtration are employed as solids removal processes. Other processes, such as ion exchange, chlorine dioxide filtration, pH adjustment and use of proprietary filter media and catalysis, have also been applied but with less frequency, owing to cost and operational considerations. Removal processes are selected on the basis of iron concentration and other conditions. There are four general methods used for removal of iron:

- The primary method involves oxidation, precipitation followed by solid transfer (sedimentation and filtration).

- The second method involves ion exchange.

- The third method involves stabilization of iron in suspension using dispersing agents to prevent the deposition of iron.

- The fourth method includes sub-surface aeration.

2.2.7.2 OXIDATION PRECIPITATION FOLLOWED BY FLOCCULATION SEDIMENTATION AND FILTRATION

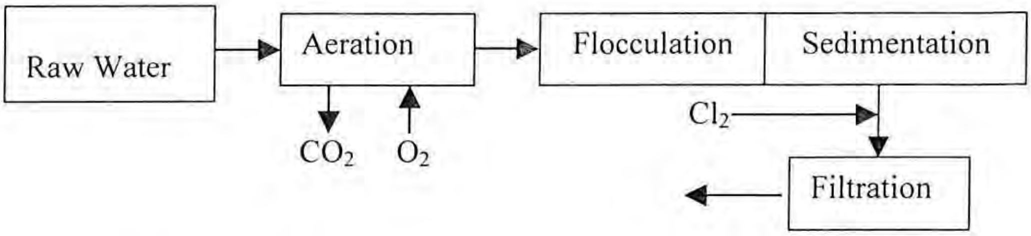
The most popular method of iron removal involves oxidation of more soluble iron(II) to relatively insoluble iron(III) and subsequent removal of the precipitates thus formed by sedimentation and filtration.

2.2.7.2.1. OXIDATION THROUGH SIMPLE AERATION

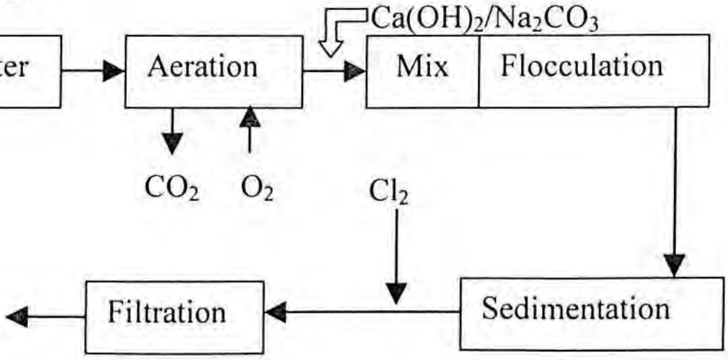
Stoichiometrically 0.14 mg/l of oxygen is required to oxidize 1.0 mg/l of Fe.

$$4Fe(HCO_3)_2 + O_2 + H_2 \rightarrow 4Fe(OH)_{3\,(s)} + 9CO_2 \text{ ....(XXIII)}$$

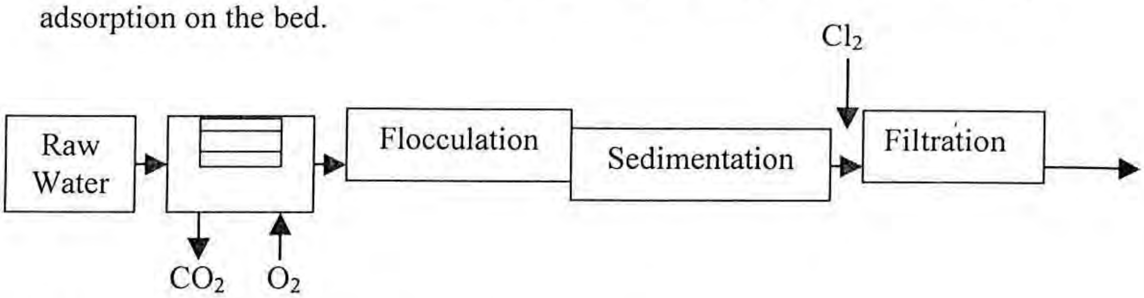
(1) Iron alone in ground water, which contains little or no organic matter with reasonable alkalinity where aerated CO_2 and H_2S are recycled raising the pH and oxidized to insoluble iron.



(2) Low alkalinity water (<130 mg/l as $CaCO_3$) needs some chemical additive to raise pH and alkalinity like lime Ca $(OH)_2$, soda ash $Na_2(CO_3)$ etc. If the water is softened by addition of lime, additional benefits include removal of iron. Aeration prior to lime addition reduces the cost of chemicals through CO_2 reduction.



(3) If the water contains organic matter and if alkalinity is low, aeration is sufficiently rapid only if it is catalysed by accumulation of oxidation products (Fe_2CO_3) on a porous bed. Iron is removed from solution by adsorption on the bed.



2.2.7.2.2 AERATION & CHEMICAL OXIDATION

In low alkaline or organic content water, the application of strong oxidizing agents such as chlorine, ozone, chlorine dioxide or potassium permanganate can serve to modify or destroy organic material and oxidize iron more rapidly. 0.94 mg/L of potassium permanganate and 0.63 mg/L of chlorine are required per 1.0 mg/L of iron respectively.

2.2.7.2.3 BIOLOGICAL OXIDATION

Gallionealla ferugina, leptothrix and other iron bacteria are capable to oxidize iron.

2.2.7.3 ION EXCHANGE

Manganese zeolite is natural green sand coated with manganese dioxide that removes soluble iron from solution. After the zeolite becomes saturated with metal ions it is regenerated using $KMnO_4$. Cation-exchange resins will remove iron.

CHAPTER 3: CHARACTERISTICS OF CLAY AND ARSENIC-IRON CONTAMINATED SLUDGE

3.1 INTRODUCTION

Characteristics of raw materials used for brick manufacturing affects on its strength, burning temperature and preparation procedure like amount of water required for preparation of brick mould, use of sand etc. These characteristics include Specific Surface Area (fineness of particles), Plastic Limit (PL), Liquid Limit (LL), Plasticity Index and Compaction. All these characteristics are interrelated and vary with type of material and moisture content. Clay alone and sludge possess dissimilar characteristics. Again blending of clay and sludge in different proportion weight reflect varying properties. Upon collection, both the sludge samples and clay were oven dried for 24 hours at 105^0C. Basic physicochemical characteristics, including moisture content, pH, and organic content were analysed for sludge and clay sample separately. Thereafter specific surface area (SSA), plastic limit (PL), liquid limit (LL) and plasticity index (PI) were analysed for sludge-clay mixtures at varying proportion (0%, 5%, 15%, 25% and 50%). Heavy metal content i.e. Arsenic, Iron, Lead and Chromium of sludge samples were determined by acid digestion with a HNO_3: HCl volume of ratio of 1:3 with a view to ascertain its toxic level. Arsenic was determined using a Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS-Shimadzu, AA-6800). Iron. Lead and Chromium were determined using Atomic Absorption Spectrophotometer (FLAAS-Shimadzu, AA-6800) by flame method.

3.2 COLLECTION OF SLUDGE AND CLAY

3.2.1 COLLECTION OF ARSENIC-IRON SLUDGE

Raw materials (Arsenic and Iron sludge) were collected from Manikganj Arsenic and Iron Treatment Plant located within Manikganj municipality. With the support from the Dutch Government, the Department of Public Health Engineering of

Bangladesh constructed eighteen arsenic removal plants in small municipalities including Manikganj by the year 1999. These plants are basically iron removal plants and add no chemicals but pump groundwater over series of cascades to aerate the water. Filtration then removes the resulting iron and arsenic co-precipitate. Then water is chlorinated and stored in an elevated tank for distribution as shown in Fig. 3.2. Water stored in the tank is periodically used to backwash the filters. The wastewater is stored in sludge ponds and sludge is removed once or twice annually. Two types of sample were collected from the previously mentioned treatment plant; Type-I; stabilized sludge (year old accumulated sludge from enclosed landfill bed) and Type-II; raw sludge (fresh sludge slurry in collection pond). Each type of sludge was stored in a separate covered plastic bucket and sealed with binding tape.

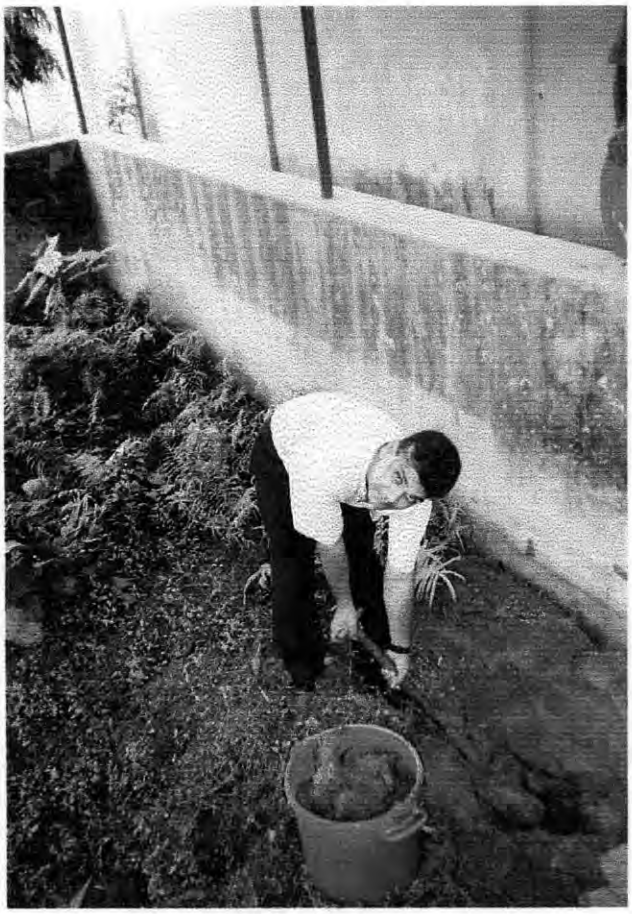


FIG. 3.1 Collection of Stabilized Sludge (year old accumulated sludge from enclosed landfill bed) from Stabilized bed (enclosed landfill bed)

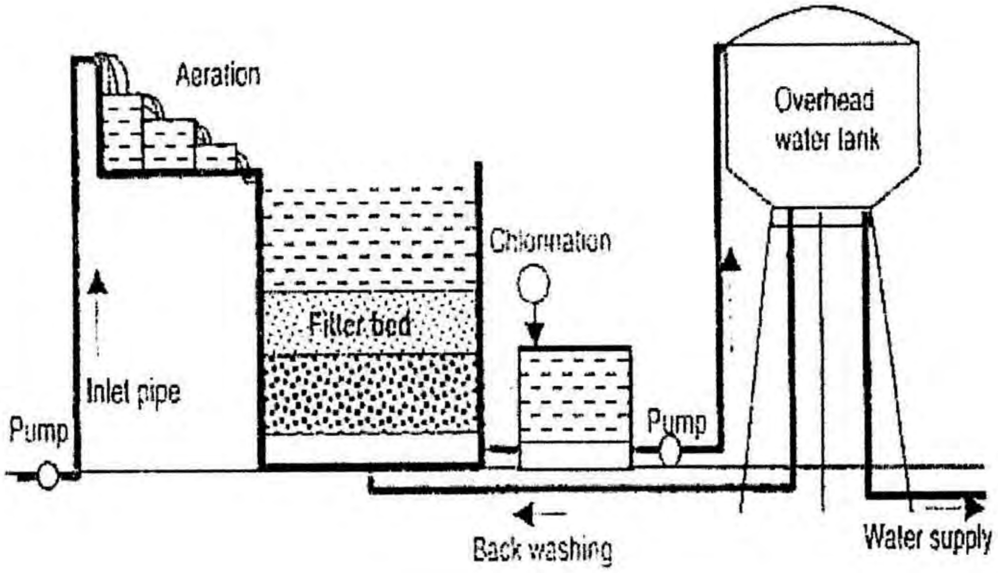


FIG. 3.2. 18-DTP Arsenic Removal Plant after (Ahmed and Rahman, 2000)

FIG. 3.3. Collection of Raw Sludge (fresh sludge slurry in collection pond) from Collection Pond

3.2.2 COLLECTION OF CLAY SAMPLE

Clay sample was collected from Mirpur Ceramic Factory Area. The factory is situated on the northwest edge of Dhaka city. Soil of this particular area is famous for preparation of various construction material i.e. hollow bricks, tiles, paving bricks, design tiles etc. Soil sample was collected from different collection site at varying depth. Sample was collected in two plastic sandbags without disturbing natural moisture content and other constituent of soil sample. Soil sample was transported upto BUET laboratory without much shock and vibration on the soil sample.

3.3 CHARACTERISTICS OF ARSENIC – IRON SLUDGE

3.3.1 PHYSICAL CHARACTERISTICS

Physical characteristics like moisture content, presence of organic compound were tested. Dry method was followed in determining moisture content of sludge samples. Sludge samples of 25 gm were taken at ambient temperature. Thereafter, samples were oven dried at 105^0C for about 24 hours. After oven drying the samples were placed in a desiccators for half an hour to cool it. After half an hour weight of the samples were taken again. Now, the reduced weight was divided with dry weight and moisture content was found in terms of percentage. Moisture of raw sludge was found to be 901.89% and the same for stabilised sludge was found to be 473.68%. Test for organic compound was carried following same procedure for obtaining moisture content with few exceptions. Wet weights of samples were taken at 105^0C oven dry condition and dry weight was taken after 550^0C oven dry for 6 hours in Carboilite muffle furnace. Following the same computation formula of moisture content, organic content of sludge samples were determined. Organic content of both raw and stabilised sludge samples were found to be only about 8.5 percent.

3.3.2 CHEMICAL CHARACTERISTICS

Chemical characteristics like pH and heavy metal content were determined for sludge sample. pH was determined with pH meter after adjusting it with standard buffer solution. pH of sludge sample was found to be 6.5. For determining heavy metal content, 5 gm of sample was taken from both type of sludges. It was then digested with aqua regia ($HCl:HNO_3 = 3:1$) for about 2.5 hours in a 500ml flask. After digestion distilled water was mixed with digested sample to make it a volume of 500 ml. On preparing this amount of sample, it was filtered with blotting paper and desired sample was prepared and collected in plastic bottle for the purpose of determining heavy metal content. Tests for arsenic, iron, lead and chromium were carried out with Atomic Absorption Spectrophotometer (AAS). Test results, as shown in Table 3.1 indicate high concentrations of arsenic and iron in the sludge, which exceed USEPA regulatory value. However, trace of lead and chromium were found in sludge sample.

TABLE 3.1. Heavy Metal concentrations in the Sludge with Drinking water Inorganic Quality Parameters (1- Stabilized sludge, 2- Raw sludge).

Constituent	**WHO Guideline (mg/l)**	**Bangladesh Guideline (mg/l)**	**Sludge (mg/kg) (105^0 oven dry)**
Arsenic^1	.01	.05	1450
Arsenic^2			2372
Iron^1	0.3	0.3	123615
Iron^2			161730
Lead^1	0.01	0.01	0.018
Lead^2			0.011
Chromium^1	0.05	0.05	0.031
Chromium^2			0.022

3.4 CHARACTERISTICS OF CLAY –SLUDGE MIX

3.4.1 SPECIFIC SURFACE AREA (SSA)

Sludge and clay samples were oven dried at 105^0C for 24 hours. Thereafter each sample was grind into dust and sieved through sieve number 100. Clay-sludge mixtures were made at 0%, 5%, 15%, 25% and 50% respectively with dust particle passing sieve 100. SSA of each mix proportion was determined following AASHTO T 153-93 (1993). As shown in Fig.3.4, the high SSA of the mixtures indicated the need for more water in the brick making process. The results of SSA obtained for the clay-sludge mixtures are shown in Table 3.2. As the amount of sludge is increased in replacement of clay, the SSA of that corresponding mixture increases proportionally. Table 3.2 also indicates that the overall particle fineness increases with the increasing percentage of sludge in the mixture.

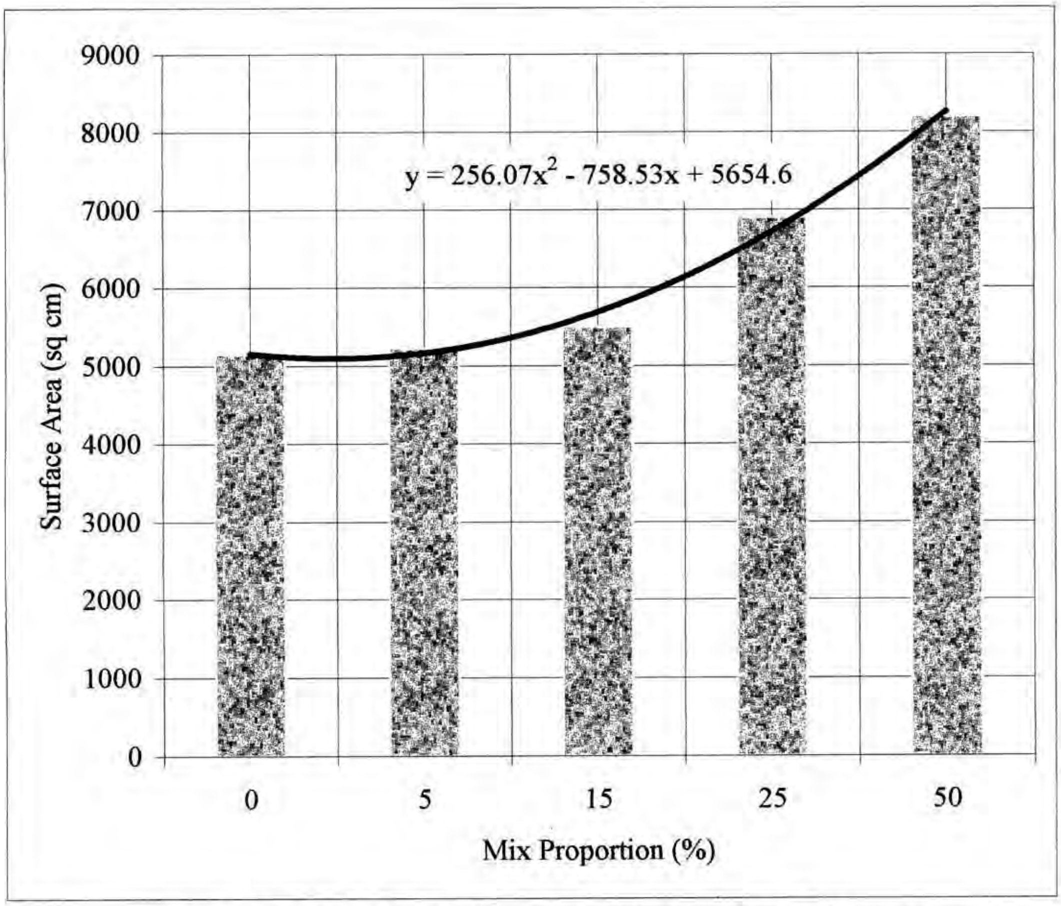


FIG. 3.4. Specific Surface Area of Sludge-Clay Mixtures

3.4.2 ATTERBERG'S TESTS

The effect of moisture on the plastic behaviour of the pulverized materials is evaluated by the Atterberg's limits test. Normally, nonplastic soil has a plastic index (PI) value ranging from 0 to 5 and 15 to 30 for a low-plasticity soil. If the PI value is greater than 35, it is classified as having high plasticity. Both air-dry sludge and clay samples were grind into finer particles and samples colleted passing sieve number 40. Clay-sludge mixtures were made at 0%, 5%, 15%, 25% and 50 % respectively. Atterberg's test of these samples were carried out following AASHTO T 89-93 (1993) for determining Liquid Limit and AASHTO T 90-92 (1993) for determining Plastic Limit. The results of Atterberg's tests of sludge-clay mixtures indicate that the value of PI is inversely proportional to the amount of sludge in the brick. A PI value of 17.97 for clay alone shows the clay can be classified as low–plasticity material. The PI values shown in Table 3.5 indicate that up to 15% of sludge can be applied to brick making without losing the plastic behaviour.

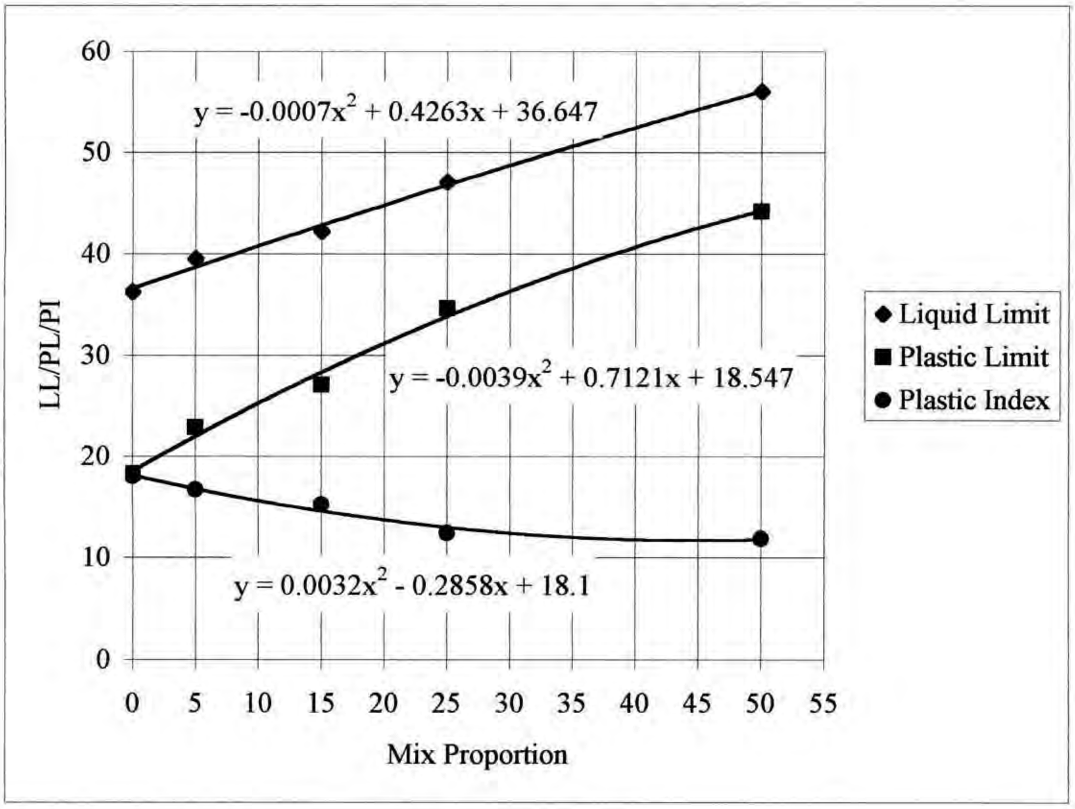


FIG. 3.5. Atterberg's Test

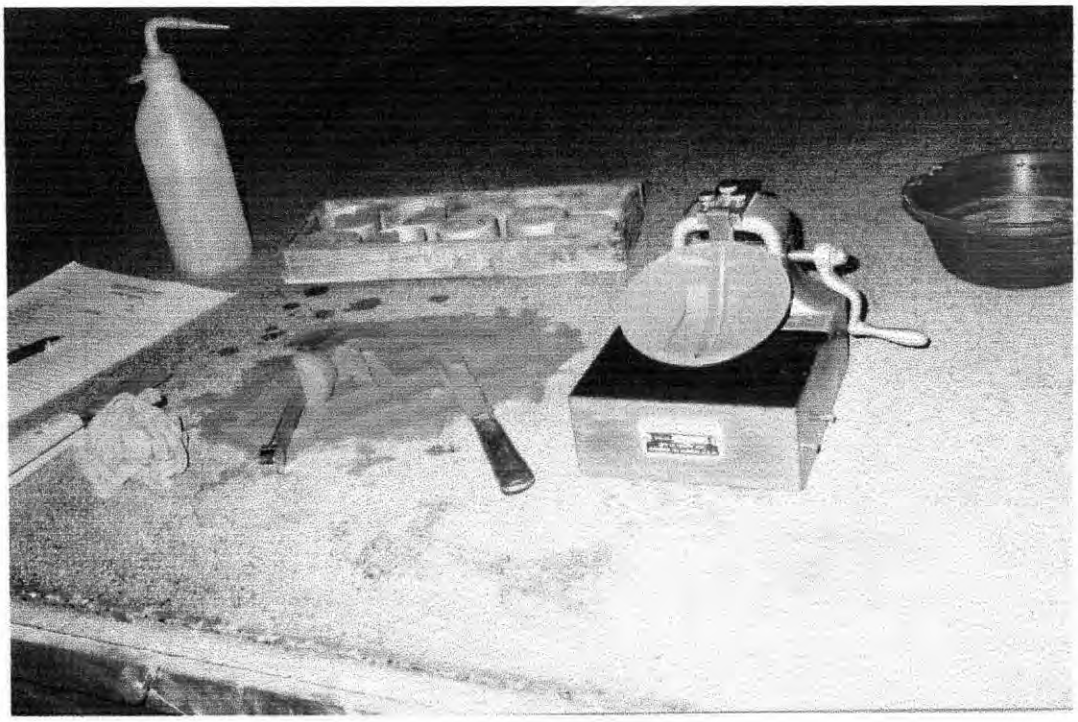


FIG. 3.6. Liquid Limit (LL) Test

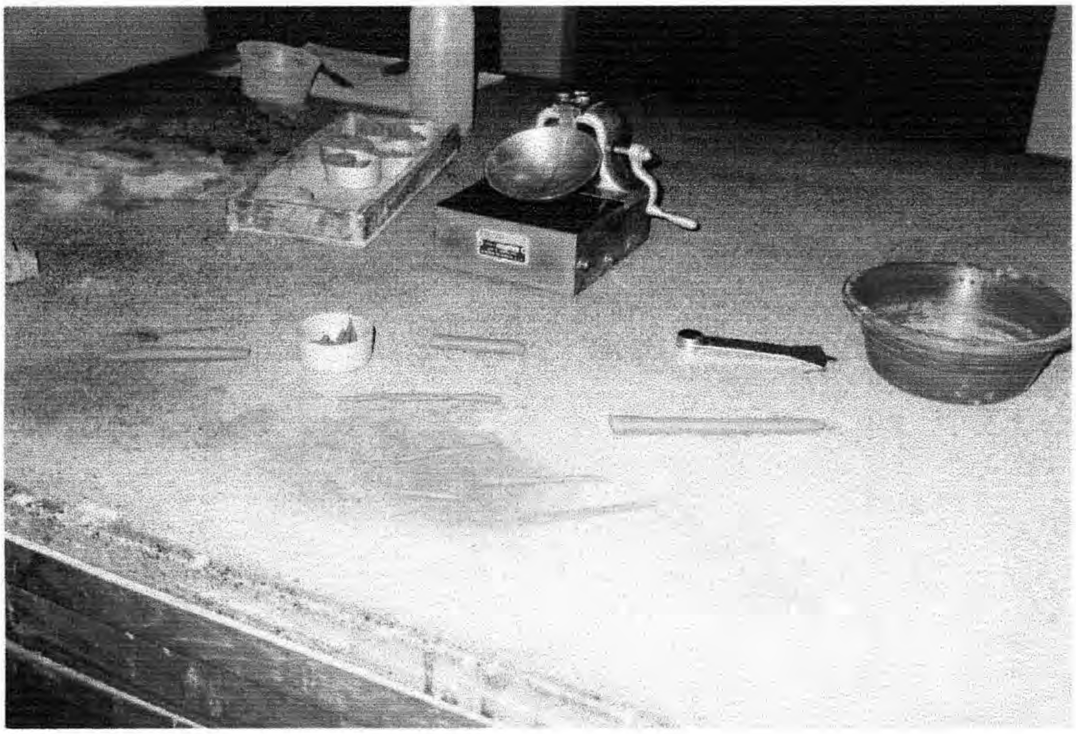


FIG. 3.7. Plastic Limit (PL) Test

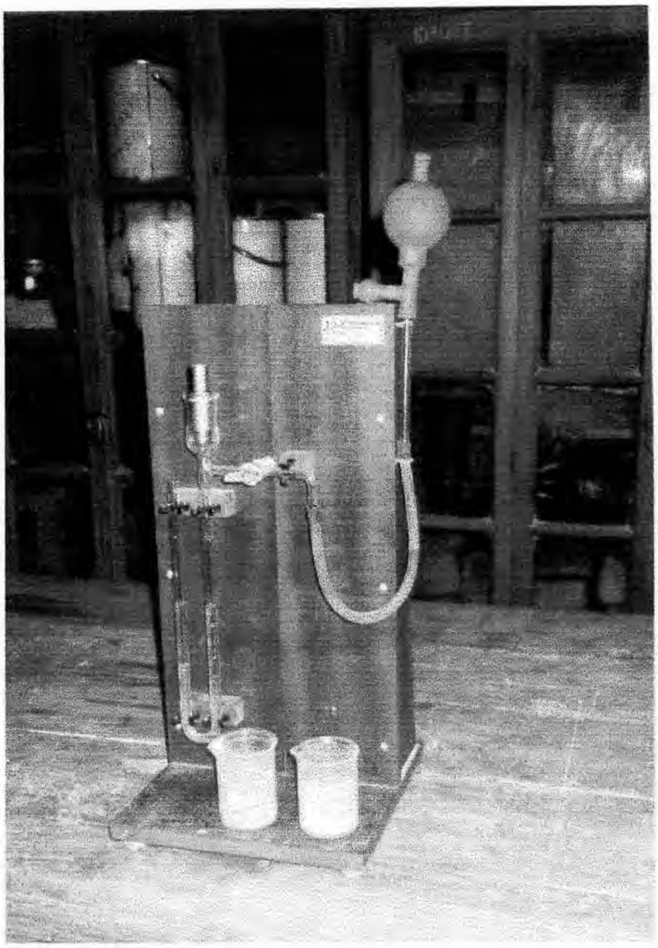


FIG. 3.8. Specific Surface Area (SSA) Test

3.4.3 COMPACTION TEST

In order to determine the OMC, which is an important factor affecting the properties of brick, a standard AASHTO T 99-93 (1993) compaction test was used in this study. Air-dry samples were grind to pass through sieve number 4. Sample amounting 25 kg for each type of mix proportion was taken to determine individual parameters of optimum moisture content (OMC) and dry density corresponding to OMC. The OMC of different mixtures was based on the moisture requirement in which maximum bonding among the mixture particles are retained. The results of AASHTO clay tests from Fig. 3.9, show that OMC is directly proportional to the increase in sludge mix in the brick and corresponding density is inversely proportional to sludge mix.

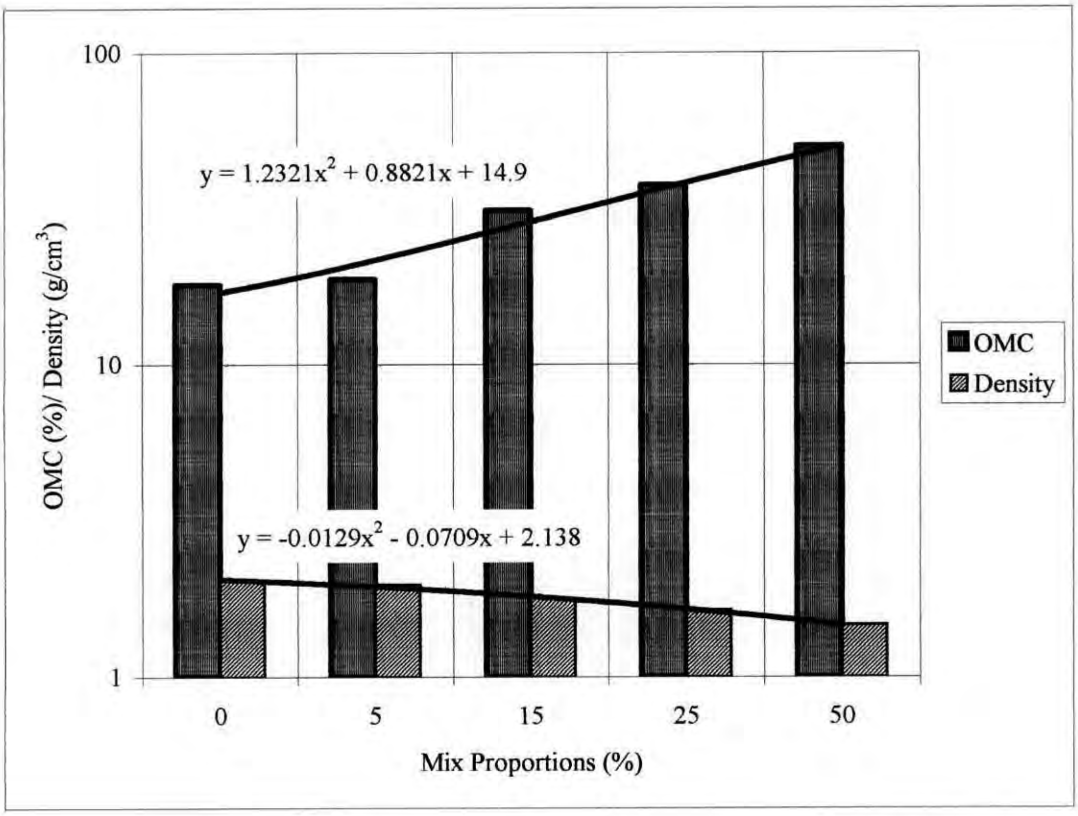


FIG. 3.9. Compaction Test of Sludge-Clay Mixtures

TABLE 3.2. Effects of Sludge Proportions on SSA, OMC, Density, Liquid Limit, Plastic Limit and Plastic Index of Mixtures.

Sludge Proportion (%)	**Specific Surface Area (cm^2/gm)**	**OMC (%)**	**Density (gm/cm^3)**	**Liquid Limit (%)**	**Plastic Limit (%)**	**Plastic Index**
0	5152	18	2.04	36.26	18.29	17.97
5	5225	18.75	1.98	39.54	22.86	16.68
15	5495	31.25	1.79	42.25	27.07	15.18
25	5906	37.5	1.64	47.08	34.65	12.43
50	6201	50	1.47	56.08	44.22	11.86

3.5 SUMMARY OF THE STUDY

Experimental result shows that the sludge has a pH of 6.5, indicating that the sludge can be treated as neutral material. Moisture content of raw sludge is 901.89% and stabilized sludge is around 473.68%, which expose sludge as quick sand with poor bearing capacity. It can also be concluded that moisture content of raw sludge is about twice than that of stabilized sludge. The reduction of moisture content might be owing to evaporation and stabilization of sludge over a period of time. Hence, it is recommended to use stabilized sludge in preparing clay-sludge mixture with a view to prepare bricks. It would lessen the possibility of acquiring uneven surface on drying bricks prepared out of sludge-clay mixtures. As shown in Table 3.1, arsenic content in raw sludge is almost double than that of stabilized sludge. It represents a similar phenomenon like moisture content of raw and stabilized sludge. Further it is observed that total arsenic concentration in both type of raw sludge is much higher than United States Environmental Protection Agency (USEPA) hazardous waste concentration limit. Test results for organic compounds shows that soil sample possess negligible amount (0.51%) organic content and sludge sample about 8.5% organic content. Experimental results from Table 3.2 indicates that mix proportion up to 15% could be used viably with a view to maintain plastic limit, working optimum moisture content and acceptable density of sludge clay mixtures.

CHAPTER 4: PREPARATION AND STANDARD TESTS OF BRICKS

4.1 INTRODUCTION

Bricks are prepared out of clay with optimum moisture content at desired burning temperature of specified burning time. A percent of sand is mixed with clay with a view to control plastic behaviour and texture of bricks. Clay is collected from ground containing clayey soil deposit. It is well mixed with water manually or mechanically (pug mill) and wet bricks prepared in a standard forma. Wet bricks are dried in ambient temperature for about seven days. Later these naturally dried bricks are burnt in the brickfield fore about 15 days. For the purpose of research, bricks replica samples were prepared in the laboratory condition. Finally half brick size was also prepared in order to obtain actual strength of original bricks size. Instead of natural drying, bricks samples were initially oven dried at 105^0C for 24 hours. Further actual burning was carried out in Carbolite heavy-duty oven (muffle furnace) for about 6 hours at constant temperature of 1000^0C, which represented 15 days total burning temperature effect on the naturally dried bricks in the brickfield (Tay, 1987).

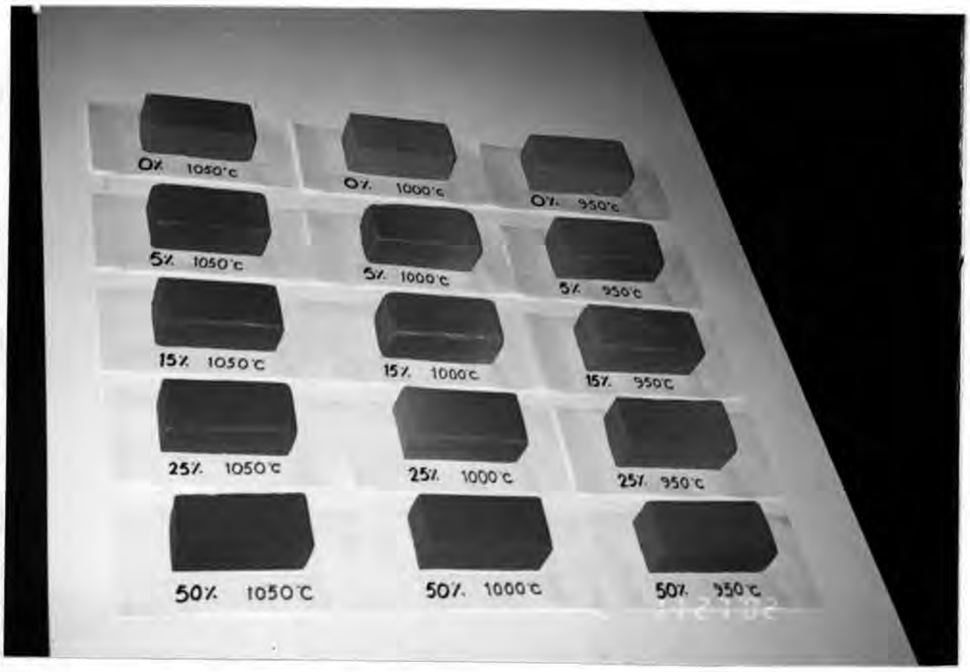


PLATE 4.1. Prepared Bricks Sample at Varying Temperatures with different Mix Proportions

4.2 PREPARATION OF BRICKS

Total 45 bricks sample (length 12.25 cm, width 5.85 cm and height 3.81 cm) of sludge-clay mixture in varying proportion (5%, 15%, 25%, 50% and 100%) at OMC was prepared in the laboratory as shown in Plate 4.1. Three clay only mixture samples were prepared as a reference specimen. All these samples were heated in Carbolite heavy-duty electric furnace at the design temperatures of 950^0C, 1000^0C and 1050^0C respectively for 6 hours as shown in Fig.4.1. Forma for the preparation of bricks sample as shown in Fig. 4.3 were prepared with corrugated steel plate. Bricks burning in Carbolite heavy-duty oven as shown in Fig 4.2 took total eight hours. Initially one hour was required in order to raise the temperature at required high temperatures (950^0C, 1000^0C and 1050^0C). Original burning period of 6 hours was maintained as shown in Fig 4.2. After six hours burning period it took again one

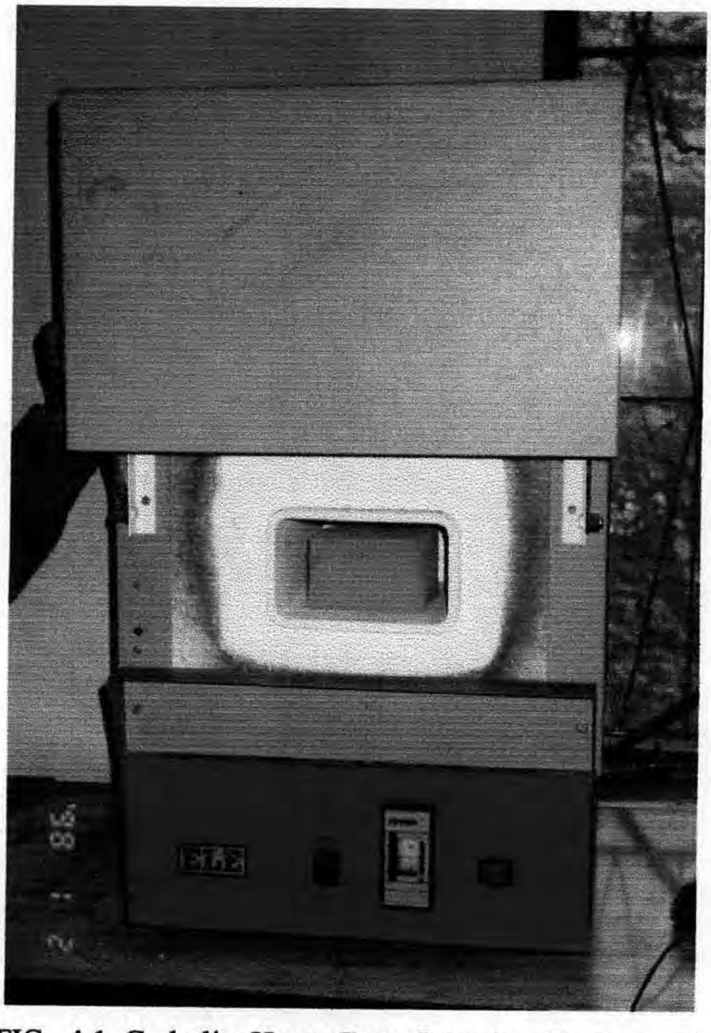


FIG. 4.1 Carbolite Heavy Duty Oven (muffle furnace)

hour to decrease temperature from high value to desired lower value. Bricks were burnt at these three temperatures with a view to obtain an accepted working burning temperature. Further, burning temperature in practical brickfield varies within above-mentioned temperatures. This peak temperature in the brickfield is obtained gradually after one-week time compared to one-hour time in the laboratory.

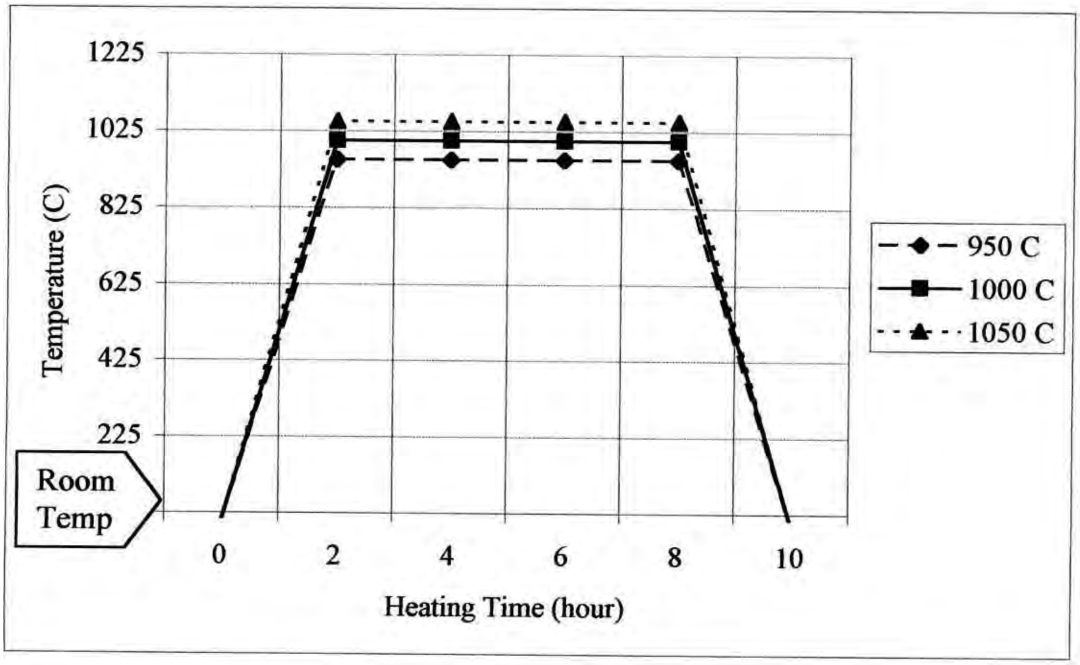


FIG. 4.2 Variation of Heating Temperature with Time

4.3 STANDARD TESTS OF BRICKS

4.3.1 GENERAL

The produced bricks then received a series of tests including firing shrinkage, weight loss on ignition, water absorption and compressive strength following BDS-208: 1980 to determine a suitable condition for producing qualified bricks. Upon determining suitable mix proportion and firing temperature of Bricks three half-size bricks were prepared since standard bricks test is carried out with half bricks. Compressive strength of these half bricks were determined and compared with replica bricks. Other physical tests include water absorption, firing shrinkage, loss of weight on ignition and density of bricks.

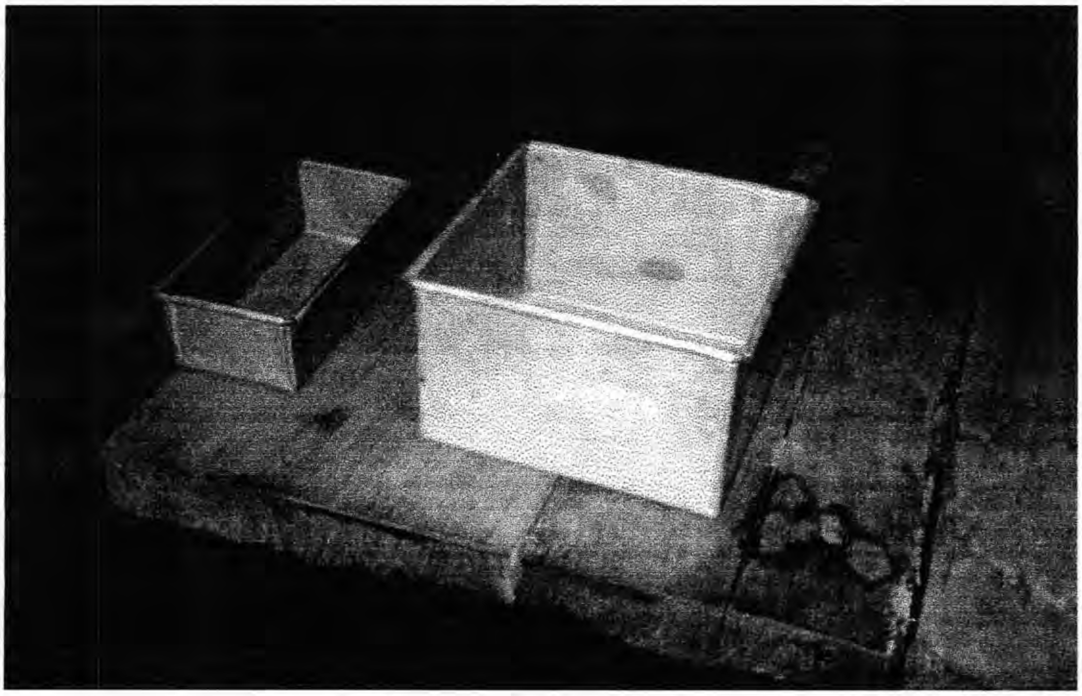


FIG. 4.3 Forma for Bricks (Replica and Half Size)

4.3.2 COMPRESSIVE STRENGTH OF BRICKS

The compression test is the most important test for assuring the engineering quality of a building material. Three bricks sample for each category were taken to test compressive strength. An average of these values was taken for each mix proportion at varying heating temperature. The results of the compressive strength test on the bricks made from both clay and sludge mixtures are shown in Fig. 4.4 and Fig. 4.5. The results indicate that the strength is greatly dependent on the amount of sludge in the brick and the firing temperature. From Fig 4.5 it is seen that compressive strength of bricks is maximum at 1000^{0}C firing temperature. From Table 4.1 it is seen that with an inclusion of 5% sludge in clay-sludge mixture, there is a decrease of strength (26.87% at 950^{0}C, 20.22% at 1000^{0}C and 26.33% at 1050^{0}C). However, this loss of strength increases remarkably with the increase of sludge mix as indicated in Table 4.1 and acceptable up to 25% mix proportion. It can be further concluded that loss of compressive strength is also minimum at 1000^{0}C. Compressive strength of bricks decreases with increase of sludge mix in the bricks but increases with the increase of firing temperature. As shown, with up to 25% sludge added to the bricks, the strength achieved at all temperatures can be as high as that of normal clay bricks. Bricks with 50 % mix proportion fall within Grade B.

TABLE 4.1. Compressive Strength of Bricks

Ser	**Sample ID**	**Firing Temp (^{0}C)**	**Mix % (As)**	**Strength (kg/cm^2)**	**Strength Ratio with Clay only Samples (%)**	**Strength Loss wrt Clay only Samples (%)**	**Half Bricks Strength (kg/cm^2)**	**Remarks**
1.	*B1*	*950*	*0*	*608.3*	*100*	*0*		Clay only bricks sample
2.	*B2*	*1000*	*0*	*718.95*	*100*	*0*		
3.	*B3*	*1050*	*0*	*692.32*	*100*	*0*		
4.	B4	950	5	444.83	73.1267	26.8733		5% Sludge mix by wt bricks sample
5.	B5	1000	5	573.52	79.7719	20.2281		
6.	B6	1050	5	510.02	73.6682	26.3318		
7.	*B7*	*950*	*15*	*362.55*	*59.6005*	*40.3995*	*353.29*	15% Sludge mix by wt bricks sample
8.	*B8*	*1000*	*15*	*440.39*	*61.2546*	*38.7454*	*449.71*	
9.	*B9*	*1050*	*15*	*391.22*	*56.5086*	*43.4914*	*386.65*	
10.	B10	950	25	260.13	42.7634	57.2366		25% Sludge mix by wt bricks sample
11.	B11	1000	25	290.85	40.4548	59.5452		
12.	B12	1050	25	407.61	58.876	41.124		
13.	*B13*	*950*	*50*	*135.18*	*22.2226*	*77.7774*		50% Sludge mix by wt bricks sample
14.	*B14*	*1000*	*50*	*147.47*	*20.5119*	*79.4881*		
15.	*B15*	*1050*	*50*	*251.94*	*36.3907*	*63.6093*		
16.	B16	950	100	45.23	10.1679	89.8321		100% Sludge mix by wt bricks sample
17.	B17	1000	100	29.87	5.20819	94.7918		
18.	B18	1050	100	0	0	100		

Bricks with 100% sludge indicate to be unsuitable for preparation of bricks. At 1000^{0}C 100% sludge converted to Jhama bricks and at 1050^{0}C it turned into ashes and broken into pieces possessing no strength.

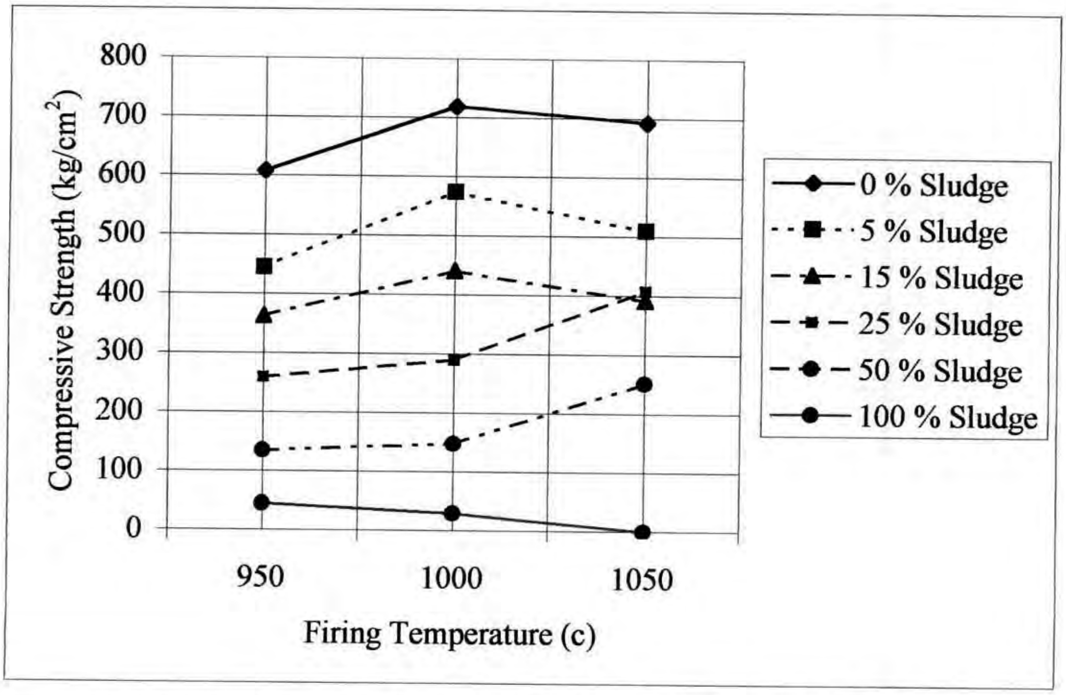


FIG. 4.4 Compressive Strength of Bricks at different Mix Proportion

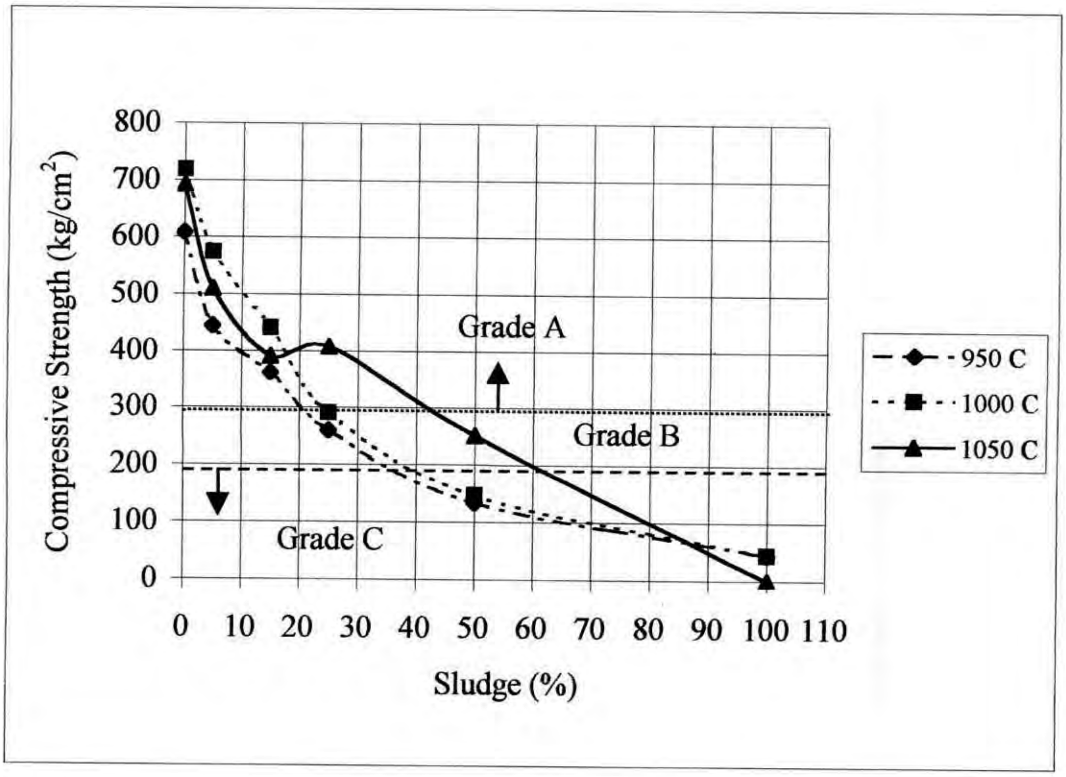


FIG. 4.5 Compressive Strength of Bricks at different Firing Temperature

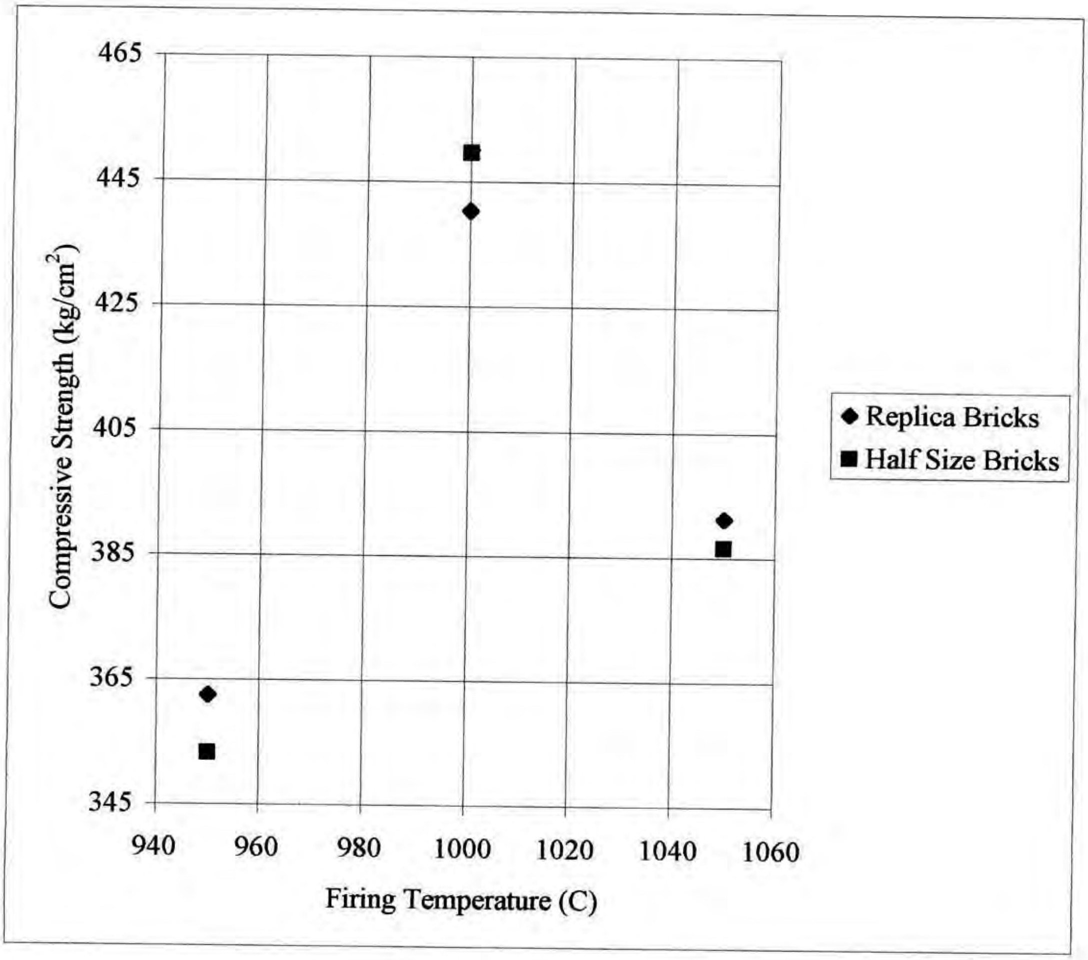


FIG.4.6 Compressive Strength of Bricks (Replica – Half Size)

The results indicated that the optimum firing temperature at which maximum compressive strengths occurred was 1000^0C for sludge mix up to 15% in the bricks. Beyond 15%, optimum firing temperature for maximum compressive strength was 1050^0C. The compressive strength of bricks made from sludge–clay mixtures all meet BDS-208: 1980 standards for brick requirements: 280 kg/cm^2 for a grade A bricks, 175 kg/cm^2 for grade B bricks and 105 kg/cm^2 for grade C bricks. Compressive strength results from Fig. 4.6 indicates that strength of half brick do not vary substantially with replica size bricks. At 950^0C and 1050^0C replica size bricks reflects higher strength than that of half bricks. However in case of 1000^0C the result is reverse and half bricks gain higher strength.

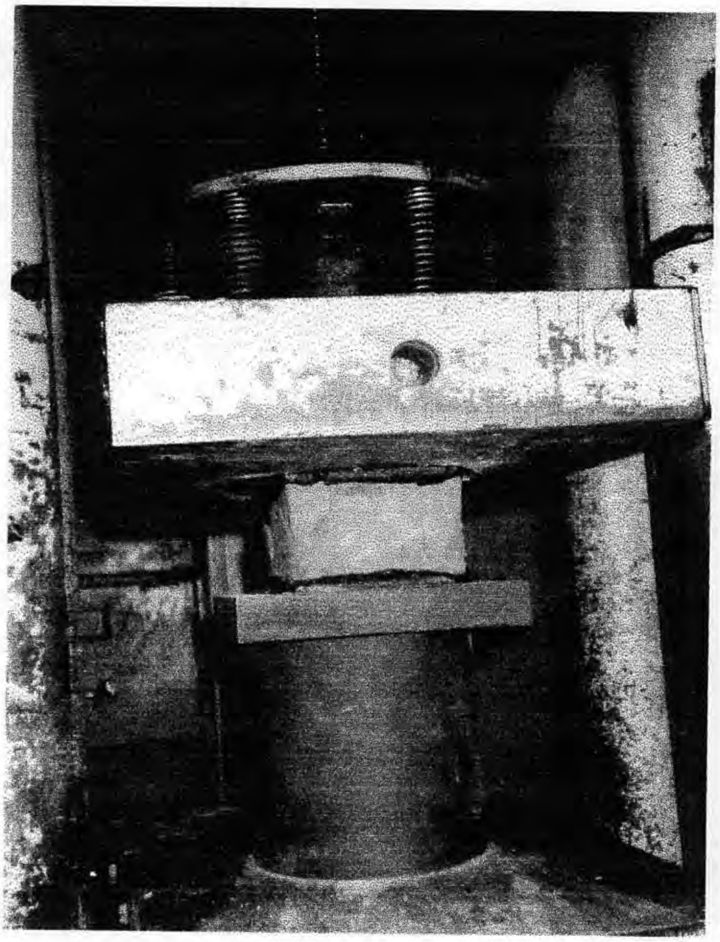


FIG. 4.7 Compressive Strength Tests of Bricks

4.3.3 LOSS OF BRICKS WEIGHT 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. In order to avoid the uneven surface texture of bricks, both sludge and clay was oven dried at 105^0C for about 24 hours. Upon drying these samples were crushed into powder and then mixed well in required proportion by weight. Fig. 4.8 shows a linear relationship between the amount of sludge to the mixture and the percent weight loss on ignition at all three temperatures. As shown, increasing the percent sludge resulted in an increase in

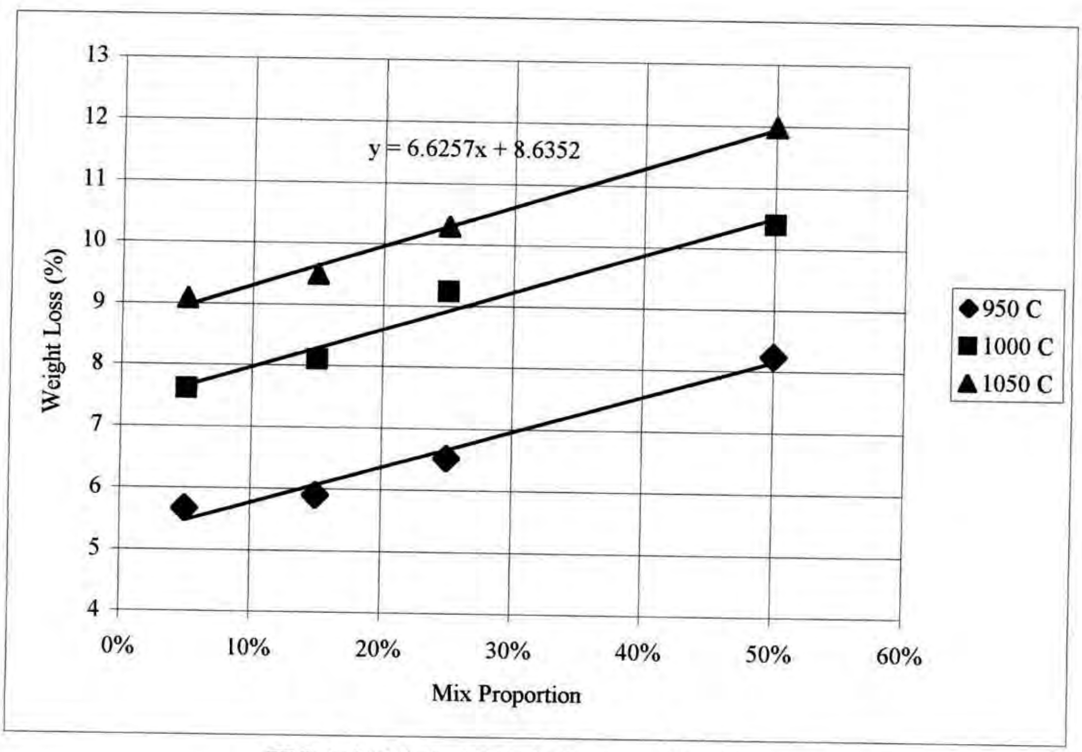


FIG.4.8 Bricks Weight Loss on Ignition

brick weight loss. The weight loss on ignition criterion for a normal clay brick is 15% (AASHTO 1982). The bricks made for this study meet all weight loss criteria.

4.3.4 BRICKS WATER ABSORPTION

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. The water absorption was determined by using the procedures described in BDS – 208: 1980. Fig. 4.9 shows the results of the water absorption tests for various sludge-clay mixtures fired at three different temperatures. As shown in Fig. 4.9, the value of water absorption is directly proportional to the quantity of sludge added. Increasing the firing temperature resulted in a decrease of water absorption, thereby increasing the weathering resistance. According to the criterion of water absorption of bricks in BDS – 208: 1980, the ratio is below 12% for grade A bricks and 12 to 16% for grade-B bricks and beyond 16% grade-C bricks. According to this guideline bricks with 15% sludge burnt at 1000 to 1050^{0}C are grade-B category and bricks with 15% sludge fired at

950^{0}C fall within grade-C category. Further, bricks with 25% sludge burnt at all temperature fall within grade-C category. However, bricks with 5% sludge fired at 1050^{0}C fall within grade-A category.

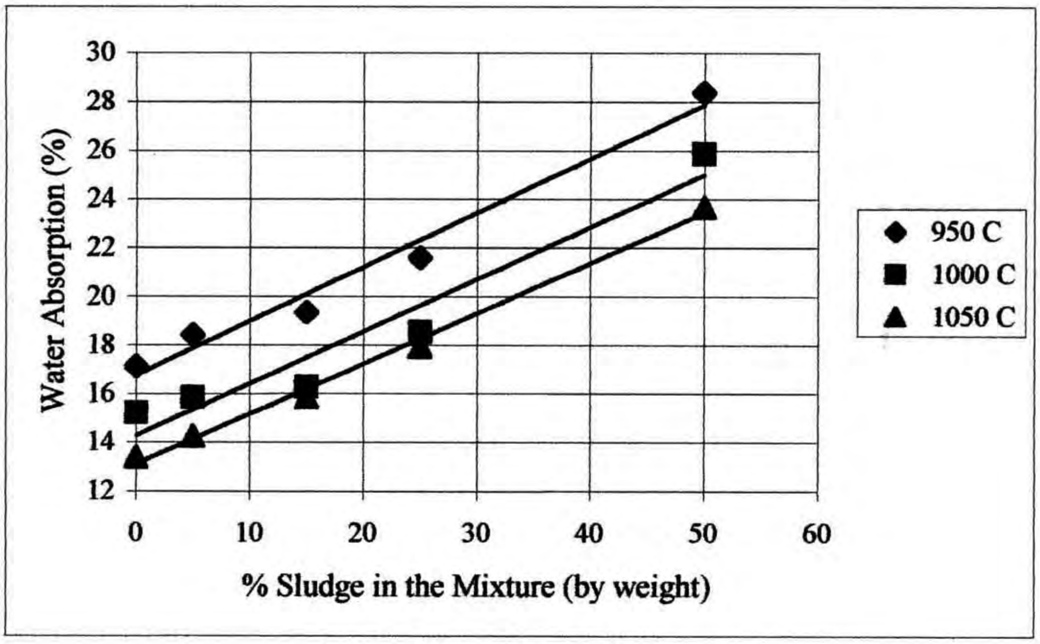


FIG.4.9 Bricks Water Absorption

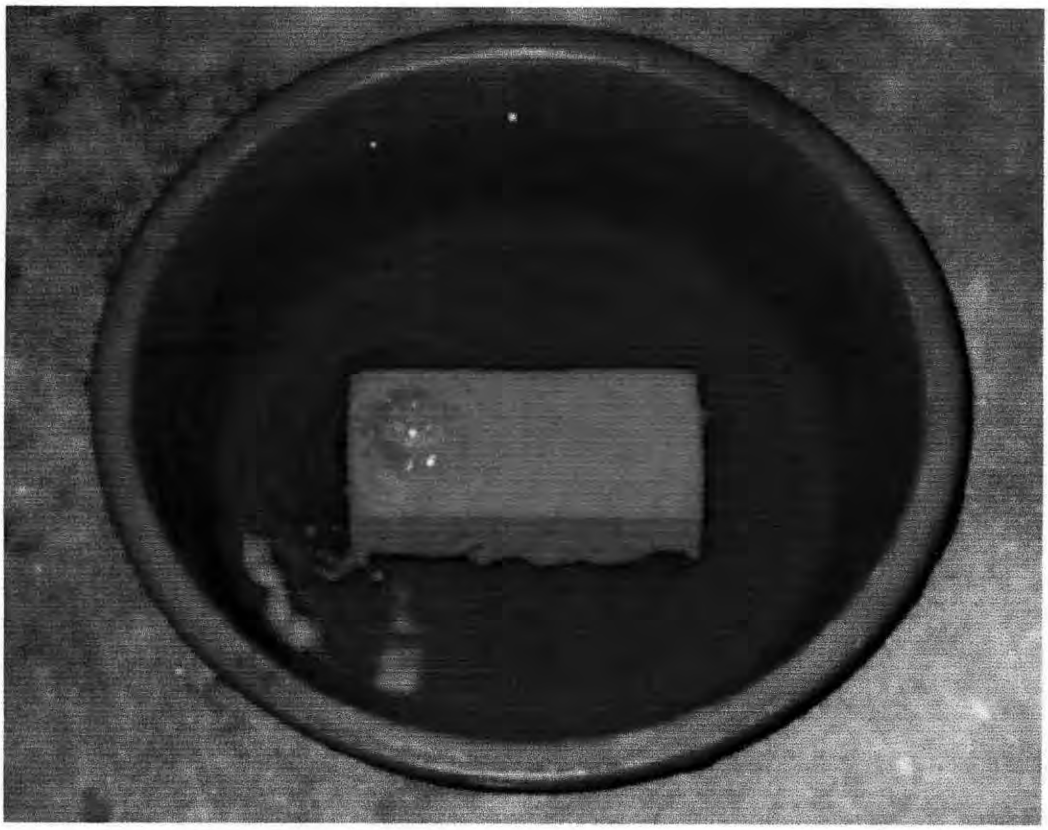


FIG. 4.10 Bricks Water Absorption

4.3.5 BRICK FIRING SHRINKAGE

The quality of brick can be assured according to the degree of firing shrinkage. Normally a good quality brick exhibits shrinkage below 8%. As shown in Fig. 4.11, the percentage of shrinkage increases as the amount of sludge is added in the mixture increases. For a normal clay brick, the shrinkage is 8.42, 10.49 and 13.9 at firing temperatures of 950, 1000 and 1050^{0}C, respectively. Firing shrinkage increase rapidly up to 15% mix proportion. However, a linear relationship between the shrinkage and the sludge proportion is observed for 15 to 50% sludge added. Because the swellability of the clay is much lower than that of sludge, an addition of sludge to the mixture widens the degree of firing shrinkage. The firing temperature is another important parameter affecting the degree of shrinkage. As shown in Fig. 4.12, in general, increasing the temperature results in an increase in shrinkage.

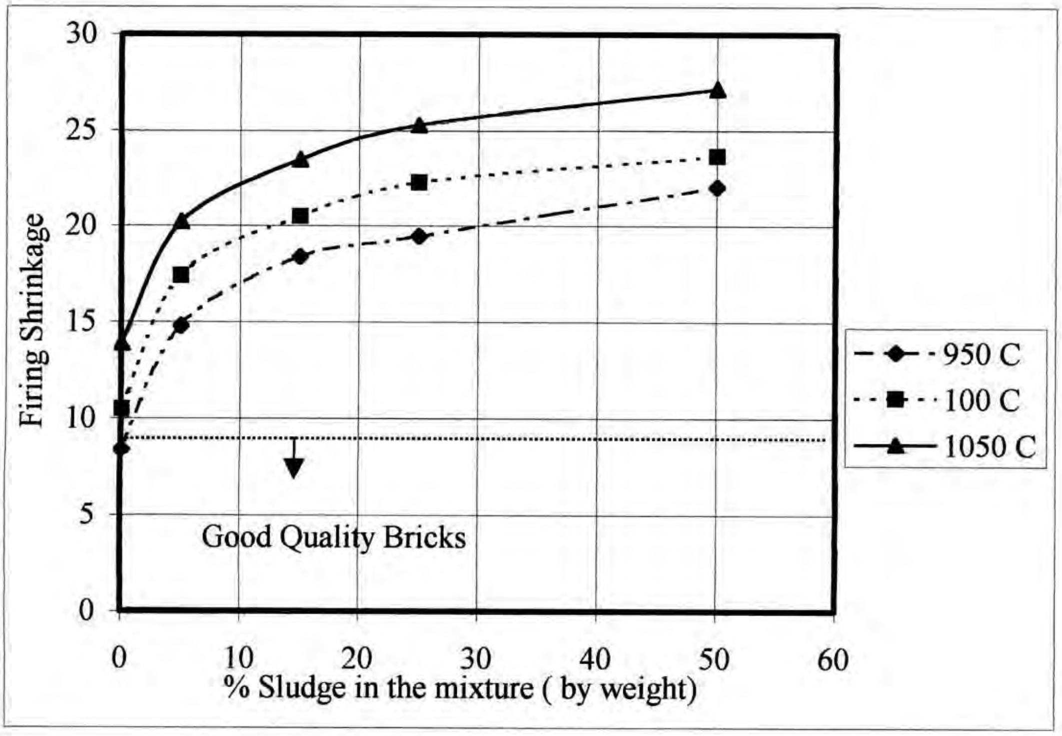


FIG.4.11 Bricks Firing Shrinkage

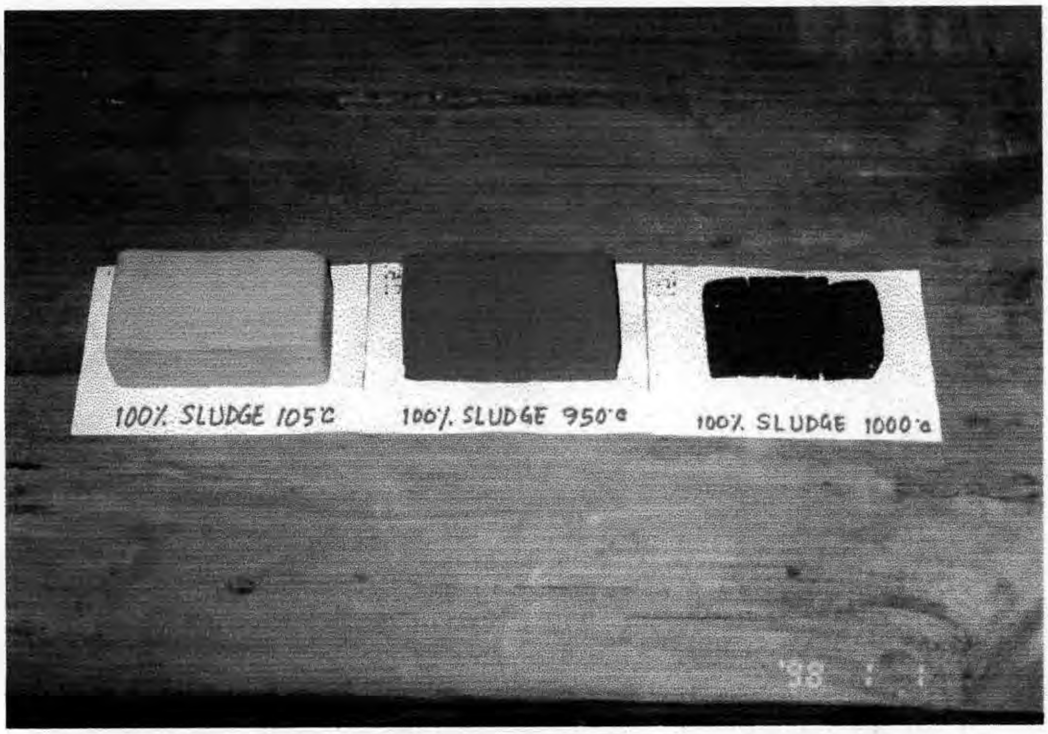


FIG. 4.12 Condition of Bricks (100% Sludge) at Varying Temperatures

4.3.6 DENSITY OF BRICKS

The bricks made with clay normally have a bulk density of 1.8 to 2.0 kg/cm^3. The measurements of bulk density for different proportions of sludge fired at three temperatures are demonstrated in Fig. 4.13 As shown, the bulk density of the bricks is inversely proportional to the quantity of sludge added in the mixture. However, up to 5% mix proportion it indicates increase in bulk density with increase of sludge mix in the clay. From 5% mix proportion and beyond a linear relationship between the bulk density and sludge proportion in the mixture for all three temperatures is observed. This finding is closely related to the quantity of water absorbed as demonstrated in Fig 4.9. When bricks absorb more water, it exhibits a large pore size than the one with less water absorption. As a result, the bulk density becomes smaller. The firing temperature can also affect the bulk density of the bricks. The results show that increasing the temperature results in an increase in bulk density.

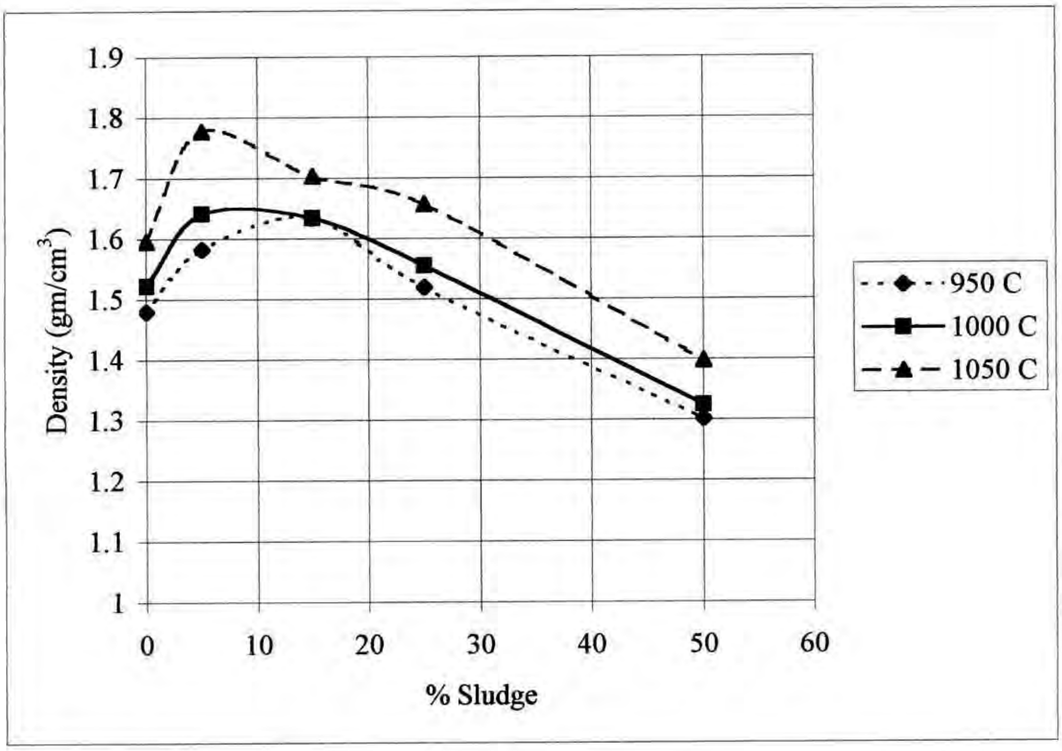


FIG.4.13 Density of Bricks

4.4 SUMMARY OF THE STUDY

The results of compressive strength tests on the bricks indicate that the strength is greatly dependent on the amount of sludge in the brick and the firing temperature. The optimum amount of sludge that could be mixed with clay to produce good bonding of bricks was 15% by weight firing at 1000^{0}C. With up to 25% sludge added to the bricks and fired at 1050^{0}C, the strength can be as high as that of normal clay bricks. The compressive strength of bricks made from sludge–clay mixtures all meets the BDS-208 (1980) brick standard. The brick manufactured did not show any deformation or uneven surfaces occurring at all firing temperatures with OMC applied in the mixtures of varying proportions. Increasing the firing temperature and decreasing the amount of sludge in the brick resulted in a decrease in water absorption. In order to yield a good quality brick, the proportion of sludge and the firing temperature are the two key factors controlling the shrinkage in the firing process. Firing shrinkage increase rapidly up to 15% mix proportion. However, a linear relationship between the shrinkage and the sludge proportion was observed for 15 to 50% sludge added. A good quality brick can be produced under the following conditions fewer than 15% sludge used and fired at 1000^{0}C. Increasing the percentage off sludge resulted in an increase in brick weight loss. The bricks made for this study all meet the criterion of 15% weight loss on ignition for a normal clay brick. The bulk density of brick was seen to be inversely proportional to the quantity of sludge added in the mixture. This finding was closely related to the quantity of water absorbed in the brick. When bricks absorb more water, it exhibits a large pore size than one with less water absorption. As a result bulk density becomes smaller.

CHAPTER 5: LEACHING TEST OF SLUDGE AND BURNT BRICKS BY TOXICITY CHARACTERISTICS LEACHING PROCEDURE (TCLP)

5.1 INTRODUCTION

The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphase wastes. If a total analysis of the waste demonstrates that individual analytes are not present in the waste or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run. If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyse the remaining fractions of the extract. If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the zero headspace extractor (ZHE) is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level (Badruzzaman, 2003).

5.2 MATERIALS AND METHODS

The Toxicity Characteristics Leaching Procedure (TCLP) in accordance with USEPA Method 1311 determined toxic characteristics of sludge. TCLP was carried out for both sludge and crushed burnt bricks sample with standard extraction fluid and varying fluid media (BUET) tap water, Rainwater and PO_4^{3-}/ SO_4^{2-}/ NO_3^-/ Cl^- mixed with distilled water. Sludge-clay mixtures were prepared at proportions of 5%, 15%, 25% and 50 %, each sample weighing 80 gm. All these samples again received high temperature heating at 950^0C, 1000^0C and 1050^0C, respectively for 6 hours. Thereafter, these burnt samples were crushed into smaller peaces for the purpose of test. Standard agitation apparatus containing six 550 ml extraction vessel rotating at 30 ± 2 rpm for 18 hours was used for the purpose of TCLP. Amount of each sample was taken as 25 gm in 500 ml extraction fluid. Acetic acid (0.57%) was used as standard extraction fluid. Constituents of varying extraction fluid are shown in Table 5.1. In preparing varying fluid media containing anion bounds as mentioned in Table 5.1 concentrations of extraction fluid were prepared keeping in view of neutral pH and acceptable highest limit of concentration of anion bounds. Extraction fluids were prepared by trial and error method maintaining pH in between 6 to 7 within maximum acceptable concentration limit of Bangladesh Drinking Water Standards for Phosphate, Chloride, Nitrate and Sulphate. Arsenic content was determined by Atomic Absorption Spectrophotometer (AAS). Each sample was tested minimum twice to obtain average value. Leaching concentration of arsenic from AAS was obtained in ppb using required dilution factor (DF). Later leaching concentration was converted into mg/kg.

TABLE 5.1. Constituents of Varying Extraction Fluids

Extraction Fluid	**Source (Salt)**	**pH**	**Mol Weight**	**Strength (%)**	**Conc (mg/l)**
BUET Tap Water	Laboratory tap water	7.06	-	-	-
Rain Water	Natural Shower	6.69	-	-	-
Phosphate ion (PO_4^{3-})	Potassium di hydrogen Phosphate (KH_2PO_4)	6.27	136.09	98.0	10
Sulphate ion (SO_4^{2-})	Sodium Sulphate (Na_2SO_4)	6.58	142.04	99.0	400
Nitrate ion (NO_3^-)	Nickel Nitrate $\{Ni(NO_3)_2. 6H_2O\}$	6.96	290.81	97.0	10
Chloride ion (Cl^-)	Sodium Chloride (NaCl)	6.04	58.44	99.5	500

5.3 RESULTS AND DISCUSSION

The results of TCLP tests from Table 5.2 indicate that leaching of arsenic from original sludge is more than that of leaching concentration of arsenic from burnt bricks. Further it was observed that arsenic leaching from stabilized sludge is more than leached arsenic from raw sludge. However leaching arsenic content is less than hazardous concentration limit i.e. 5mg/L but much more than Bangladesh drinking water inorganic quality parameter i.e. 05 mg/L (Eriksen et al., 2001). Further from Fig. 5.1 it is observed that leaching increases with the increase of sludge mix and decreases with firing temperature. However, the decrease is prominent with 5% to 15% sludge mix. From Table 5.2 it is seen that leaching of arsenic is independent of concentration of arsenic in between mix proportion of 15% to 50%. It is further observed that variation of leaching is insignificant at high firing temperatures i.e. 950^0C, 1000^0C and 1050^0C at all mix proportions. Thus, it can be concluded that during the TCLP, constituents are extracted from the waste to simulate the leaching actions that occur in landfills.

TABLE 5.2. Result of TCLP Tests of Sludge and Bricks Samples With Standard Extraction Fluid (1-Stabilised Sludge, 2- Raw Sludge)

Mix Proportion (%)	**Heating Temperature (^{0}C)**	**Leached As (mg/kg)**	**Mix Proportion (%)**	**Heating Temperature (^{0}C)**	**Leached As (mg/kg)**
100[1]	105	3.558	25	1000	2.3668
100[2]	105	2.1916	15	1000	2.2384
50	950	2.3844	5	1000	1.0388
25	950	2.3376	50	1050	2.36
15	950	2.292	25	1050	2.3148
5	950	0.9864	15	1050	2.234
50	1000	2.4696	5	1050	0.996

From Fig. 5.2 it is seen that leaching of arsenic is maximum at 1000^0C firing temperature at all mix proportions. Results from Table 5.2 also indicates that variation of leaching between sludge sample and burnt bricks is not very prominent though leaching rate of burnt bricks sample is lower than that of sludge sample alone. As such, it may be concluded that TCLP test is not an appropriate method for waste containing arsenic likely to leach hazardous concentrations of particular toxic constituents into the groundwater as a result of improper management.

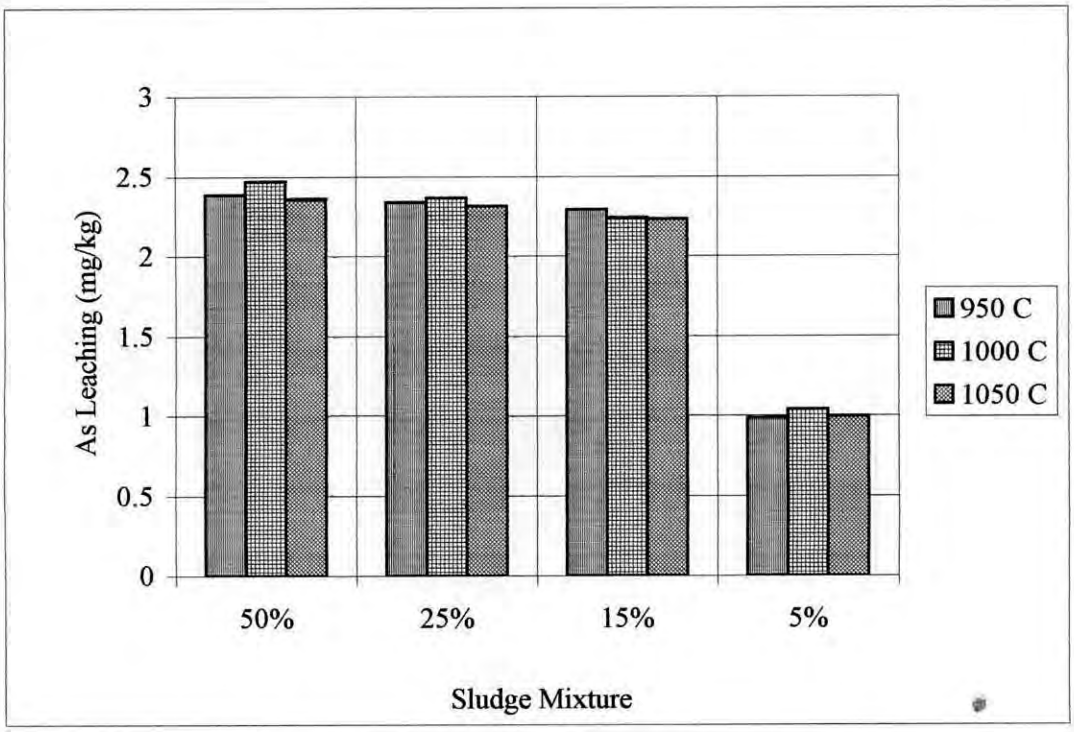


FIG. 5.1. TCLP of Crushed Burnt Samples (Varying temperature)

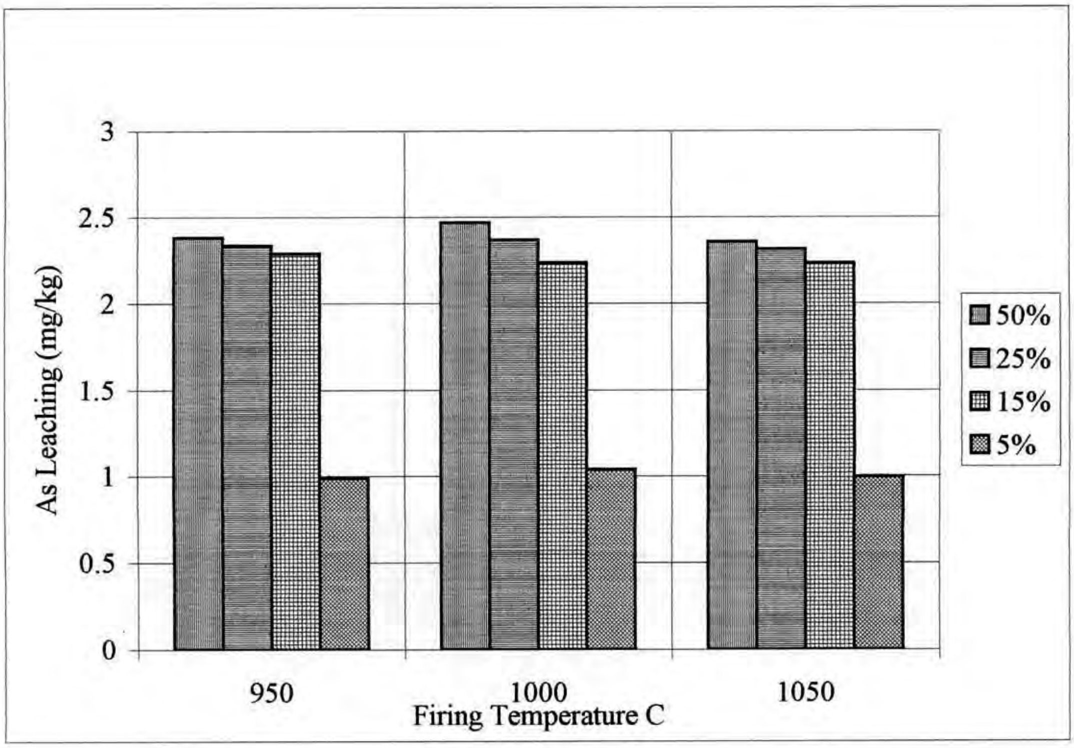


FIG. 5.2. TCLP of Crushed Burnt Samples (Varying mix proportions)

The results of TCLP tests from Fig. 5.3 indicate that leaching of arsenic from burnt bricks sample is lower than that of sludge sample though not very prominent in varying extraction fluid media. Results from Table 5.3 indicate that arsenic-leaching concentrations varies in different media condition. Leaching of arsenic is more in rainwater extraction fluid than ground water extraction fluid. Further higher value of leaching is observed in case of extraction fluid containing Phosphate and Chloride anion than fluids containing Nitrate and Sulphate anion. It is also seen from Fig 5.3 that, leaching of arsenic is more than that of natural water in case of extraction fluid containing individual anion bounds like phosphate, chloride, nitrate and sulphate. Thus it can be concluded that combined effect of all anion bounds are likely to effect reduced leaching of arsenic than that of individual anion bound.

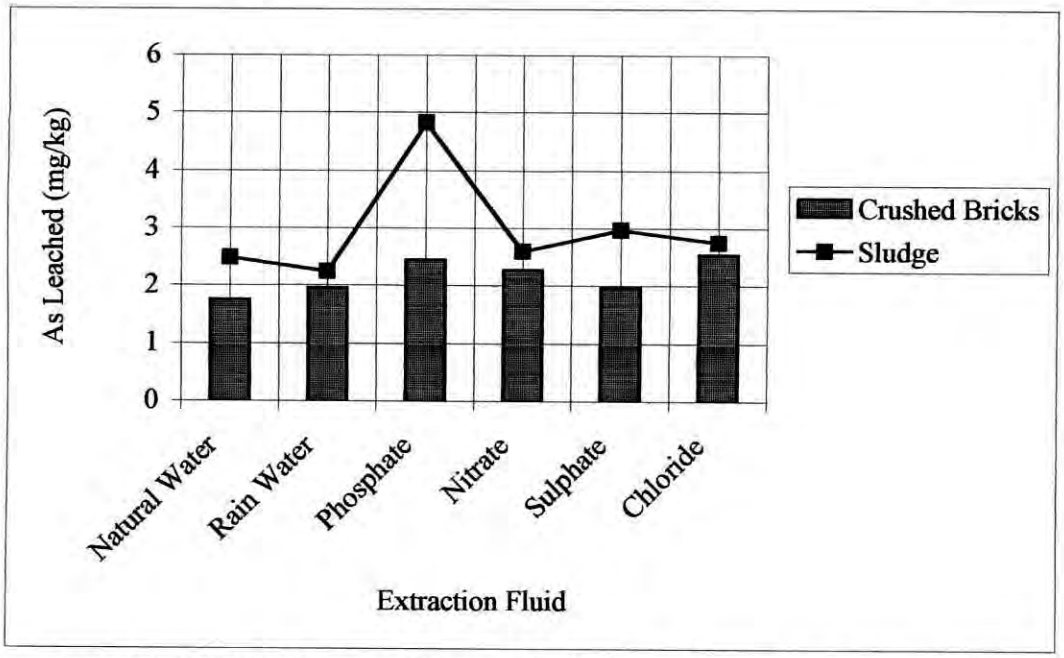


FIG. 5.3 TCLP of Crushed Bricks and Sludge in Varying Extraction Fluids

TABLE 5.3. Result of TCLP in Varying Fluid Media

Fluid Media	**BUET tap Water (mg/kg)**	**Rain Water (mg/kg)**	**PO_4^{3-} (mg/kg)**	**SO_4^{2-} (mg/kg)**	**NO_3^- (mg/kg)**	**Cl^- (mg/kg)**
Sludge Sample	2.48	2.24	4.832	2.59	2.976	2.7553
Crushed Bricks	1.7412	1.9544	2.448	2.272	1.9684	2.5348

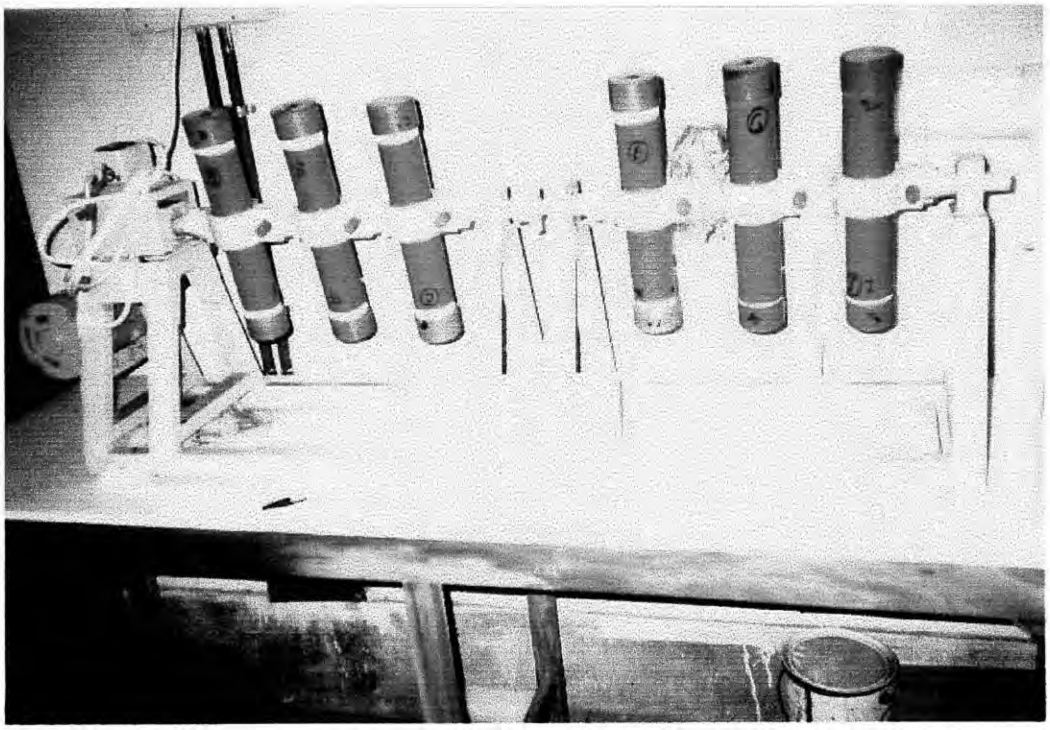


FIG. 5.4 TCLP Agitation Apparatus

5.4 MASS BALANCE ANALYSIS OF TCLP

5.4.1 GENERAL

Arsenic content in sludge is dissipates in various ways. Major causes include biomethylation (natural and artificial), stabilisation, desorption and leaching. Hence mobility of arsenic in the environment plays a vital role in its mass balance. Mass balance of arsenic content in sludge-clay mixture at different proportions burnt at 1000^0C was carried out in four steps. Initially arsenic content of sludge-clay mix of 80gm was determined at varying proportions of 5%, 15%, 25%, 50% and 100%. Thereafter all these samples were burnt at 1000^0C and arsenic content of all these samples were determined. On determining arsenic content of burnt samples, TCLP of each samples were carried out with TCLP agitation apparatus. Extracts were collected in 250ml plastic bottles. Having collected the extracted fluid (fluid containing leached arsenic) arsenic content of extracted fluid and leftover samples after TCLP was determined separately.

TABLE 5.4. Arsenic Content in different Environment (Mass Balance)

Ser	Arsenic Content (mg/kg)	Mix Proportion				
		100%	50%	25%	15%	5%
1	Sludge	1450.2	725.1	362.55	181.275	96.63
2	After Burning	515.164	202.84	96.686	65.537	27.556
3	TCLP Extract	73.49	61.64	59.17	55.96	25.97
4	As after TCLP	398.54	137.25	36.92	8.65	1.39

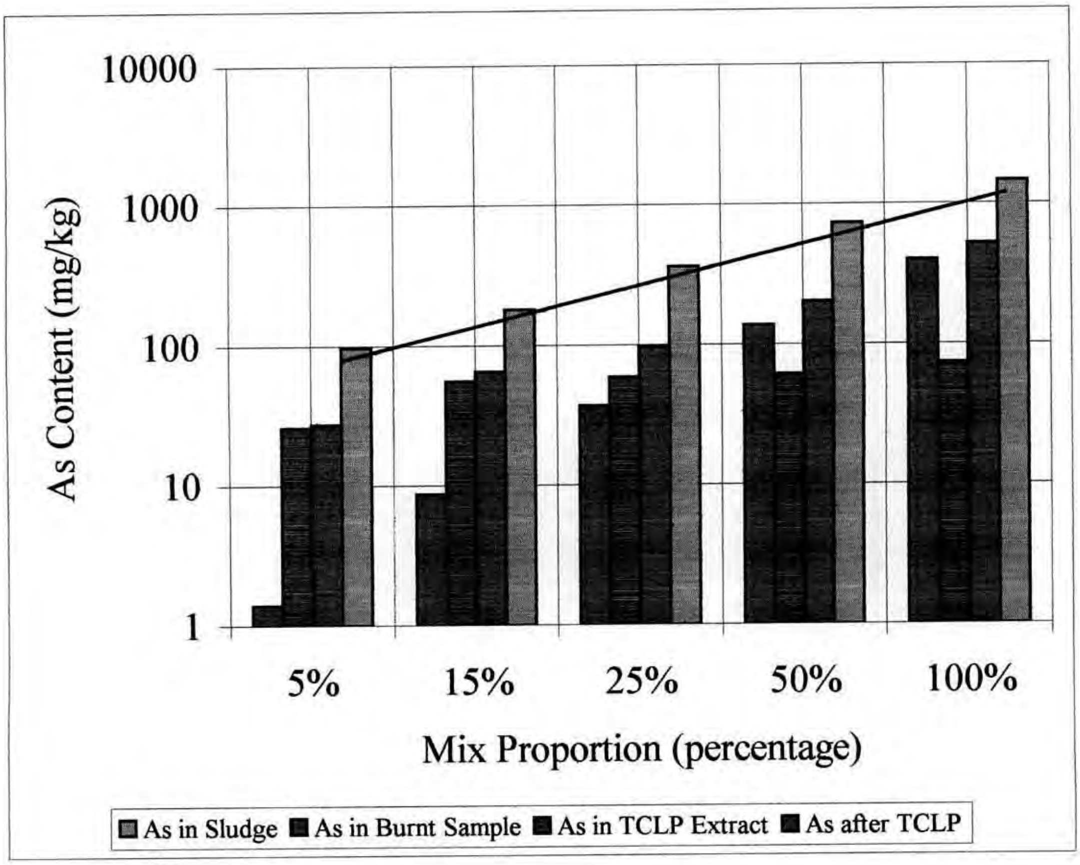


FIG. 5.5 Mass Balance Analysis

5.4.2 RESULTS AND DISCUSSION

Arsenic content in various mixes proportions with varying environmental conditions represent dissimilar value. The proportionate decrease or increase of arsenic content in raw sludge-clay mix and after burning shows remarkable difference. On burning a handsome amount of decrease in arsenic content is seen. On the other hand arsenic content variation is bare minimum with variation of mix proportion in case of leached extract of arsenic from sludge. However, arsenic content in residual sample after carrying out TCLP reflects similar result like arsenic content of burnt sample. It is further observed that arsenic content after burning is sum of leached arsenic and residual arsenic in the sludge after TCLP as shown in Fig 5.5. It is further observed from Table 5.4 that, burning of mixes of varying proportions enhances biomethylation of arsenic. Hence, it can be concluded that burning of arsenic sludge is an aid to the control of arsenic mobility in geochemical environment.

5.5 SUMMARY OF THE STUDY

In the brick making process, the sludge and clay are all fired up to 950 to 1050^{0}C. At such temperatures, the formation of metal oxides minimizes the leaching of metals. As shown in the results of TCLP tests from Table 5.3, the quantities of arsenic leached from burnt sludge are all less than those from in the dried sludge. This can be attributed to the metal form (Fe) in the sludge that has been converted to oxides during heating at high temperature. Arsenic co precipitate with iron and a process of cementation occurs between these two substances. TCLP results from Table 5.3 indicate a similarity between leaching of both sludge sample and burnt bricks. In both cases leaching concentration from burnt bricks is seen to be smaller than leaching concentration from sludge samples. It is also seen that leaching in rainwater fluid media is more than tap water. It can be concluded that rainwater possess lower pH value than that of tap water resulting higher leaching from both sludge and bricks sample. TCLP result does not indicate sludge as hazardous material. These results recommend that USEPA TCLP may not be suitable for assessment of long-term leaching from arsenic laden waste as such leaching may be kinetically directed. Mass balance analysis indicates a considerable amount of difference in arsenic content in arsenic laden sludge after and before burning. Mass balance before burning and after burning is dissimilar. It also indicates that burning is an aid to reduce arsenic pollution in the environment.

CHAPTER 6: COLUMN LEACHING OF SLUDGE-SOIL MIX

6.1 INTRODUCTION

The Toxicity Characteristics Leaching Procedure (TCLP) is primarily performed for screening of wastes for toxicity/reactivity and to determine the stability of the waste for the pollutants under consideration (Badruzzaman, 2003). Aggressive leaching adopted in TCLP at pH ≤ 5 when applied to the waste collected from different arsenic removal units has not produced leachate concentrations significant enough to term the wastes toxic as per the USEPA regulatory levels. However, TCLP may not be suitable for assessment of long-term leaching of arsenic from arsenic-rich waste, because such leaching may be kinetically restricted. Thus, modification of TCLP to represent the natural leaching environment comparable to real disposal conditions is necessary. Column is aimed at carrying out long term leaching from arsenic laden waste. Hence column leaching may be kinetically directed. Leaching is dependent on duration of contact, contact area and pH. In the absence of standard method for long time leaching column-leaching technique with avail resources serve as a fruitful alternative employing improvisation in model set up and operation. Column leaching takes longer time than that of TCLP, but it provides better performance in assessing leaching concentration from arsenic laden waste.

6.2 MATERIALS AND METHODS

Fluids of varying composition were allowed to drip through 100 ml burette from 9-litre plastic water container placed at higher elevation on a table being connected by plastic tube as shown in Fig 6.1. Five burettes were filled up with 35 gm sludge sample (105° C oven dry) and one burette with 75 gm burnt brick samples. Improvised filter arrangement was made at the bottom of burette with stone chips comprising size 4,8 and 16. Extraction fluid media were prepared by trial and error mixing proportions with a view to adjust pH within normal range in between 6 to 7.5 as shown in Table 5.1. BUET tap water was used as fluid media for burnt bricks sample and one set of sludge sample. Fluids containing Phosphate, Nitrate, Sulphate and Chloride anion were used for rest four sets of sludge samples. Extraction fluids were collected at 6-litre water bucket placed beneath each burette. Concentrated HCl of 1 ml was added to each collected extraction fluid to ensure that arsenic remains soluble in the collected solution. Continuous flow of fluids was maintained by regular refilling of container in each week as and when necessary. Uninterrupted constant flow rate of fluids were maintained by adjusting dripping cock of individual burette. Leaching fluids samples were collected in 60 ml plastic container at interval of 24 hours to 7 days being dependent on flow rate of fluid media. Arsenic content was determined by graphite furnace Atomic Absorption Spectrophotometer (GFAAS). Phosphate content was determined by Spectrophotometer DR/4000 using procedure Orthophosphate method (HACH procedure – 3025). Sulphate content was determined by Spectrophotometer DR/4000 using procedure Sulpha Ver 4 method (HACH procedure – 3450). Nitrate content was determined by Spectrophotometer DR/4000 using procedure Cadmium Reduction method (HACH procedure – 2530). Chloride content was determined following Mohr method employing silver nitrate as the titrant and potassium chromate as the indicator.

FIG. 6.1. Column Leaching Apparatus

6.3 RESULTS AND DISCUSSION

6.3.1 GENERAL

The results of column leaching tests from Fig. 6.2 indicate that leaching of arsenic from burnt bricks is much higher than leaching concentration of original sludge at initial stage. However, leaching from bricks sample sharply decreases and continues to decrease further gradually as duration of leaching progresses. In case of leaching from sludge through different fluid media, it is observed that leachate concentrations from sludge moves in a bandwidth as duration increases. However, within the bandwidth leachate concentration from phosphate (PO_4^{3-}) anion shows maximum value. Cumulative leachate concentrations from Fig.6.3 indicate that leaching from bricks sample continue to increase in much lower rate than that of leaching from sludge samples. As duration progresses, rate of increase of leachate concentration from bricks sample leads almost to negligible value and maintains a steady state. In case of leaching from sludge sample, it is observed that rate of increase in leachate concentration from PO_4^{3-} anion fluid media is much higher than SO_4^{2-}, NO_3^- and Cl^- anion fluid media. Leachate concentration from BUET tap water media shows that individual anion fluid media cause increase rate of arsenic leaching than that of combined effect of all anions present in a fluid media. An interesting relation between leachate concentration and dripping volume of extraction fluid media is found. It is seen that with high dripping volume leachate concentration decrease and increase with lower dripping volume.

6.3.2 CORRELATION BETWEEN COLUMN LEACHING AND TCLP

Results of Arsenic leachate concentration from TCLP and Column leaching indicate that leachate concentration from Column leaching reflects a comprehensive and better result than that of TCLP. In case of TCLP leachate concentrations from both sludge and burnt bricks were considered to be well below USEPA regulatory value (5 mg/L) though leachate concentrations from sludge samples were all along higher than that of leachate concentration from burnt samples. In case of Column leaching it is seen that leachate concentration from sludge crossed USEPA regulatory value onward 6th day of leaching, though initial leaching of sludge samples were much lower than that of bricks as shown in Fig 6.3. However, in both TCLP and Column leaching technique phosphate anion extraction fluid shows to cause higher leachate concentration than other types of extraction fluid media.

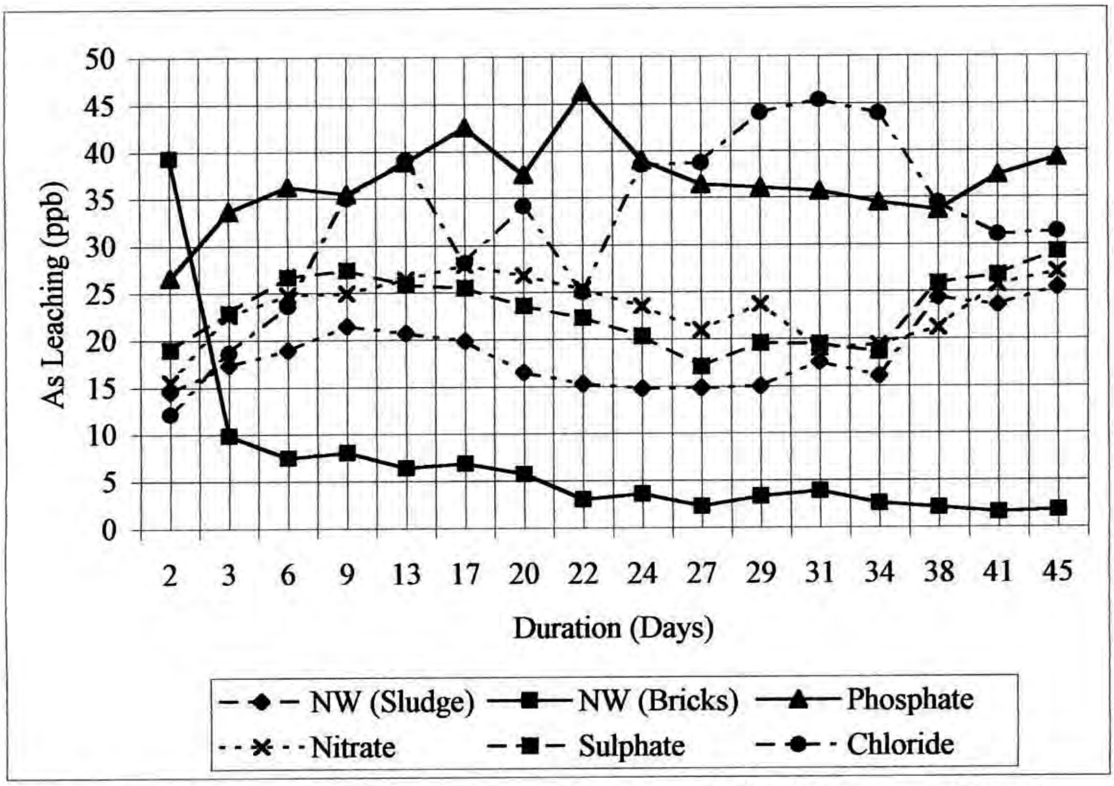


FIG. 6.2 Column Leaching in Varying Fluid Media (Individual Strength Value)

6.3.3 CORRELATION BETWEEN ARSENIC LEACHING AND RESIDUAL PHOSPHATE

10 mg/l of phosphate was used in phosphate anion containing extraction fluid media. From residual concentration of phosphate as shown in Fig. 6.4 it is seen that residual concentration of phosphate is much lower than that of input concentration. Further it indicates that arsenic leachate concentrations increase with higher residual phosphate concentration. Thus it appears that phosphate possess an affinity towards arsenic. Hence, use of increased fertilizer in the paddy field might cause increased arsenic leaching in the soil environment.

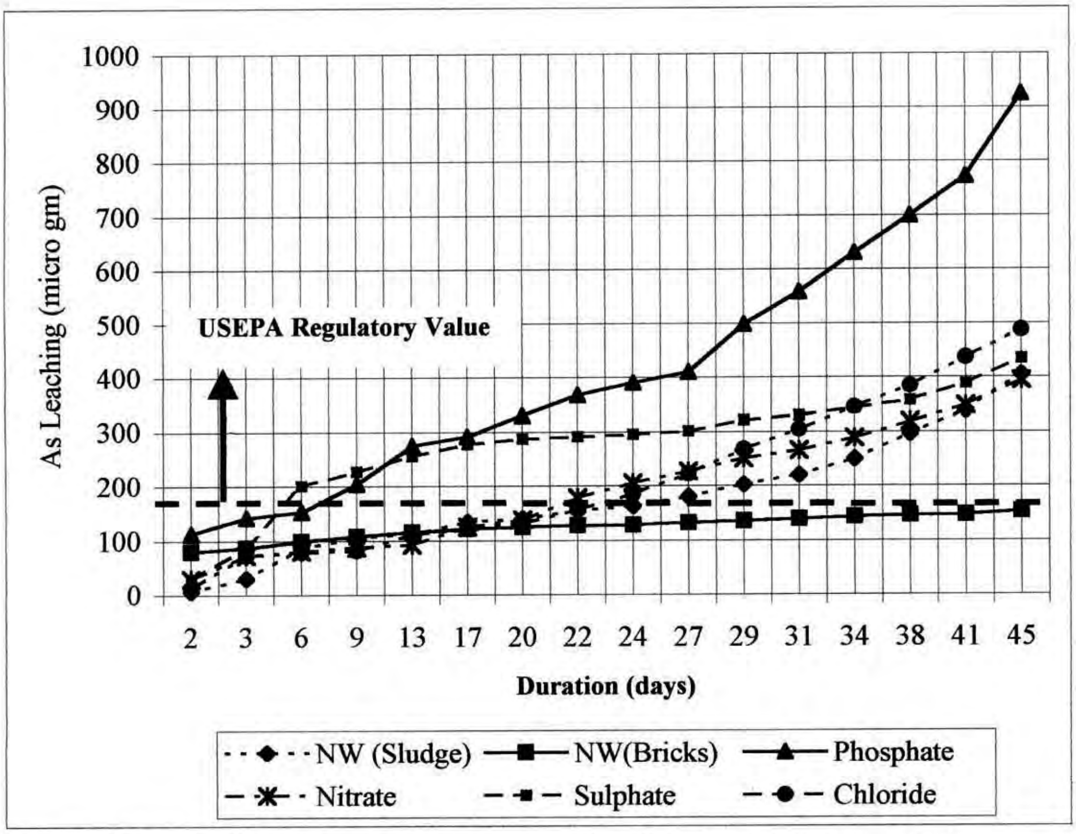


FIG. 6.3 Column Leaching in Varying Fluid Media (Cumulative Value)

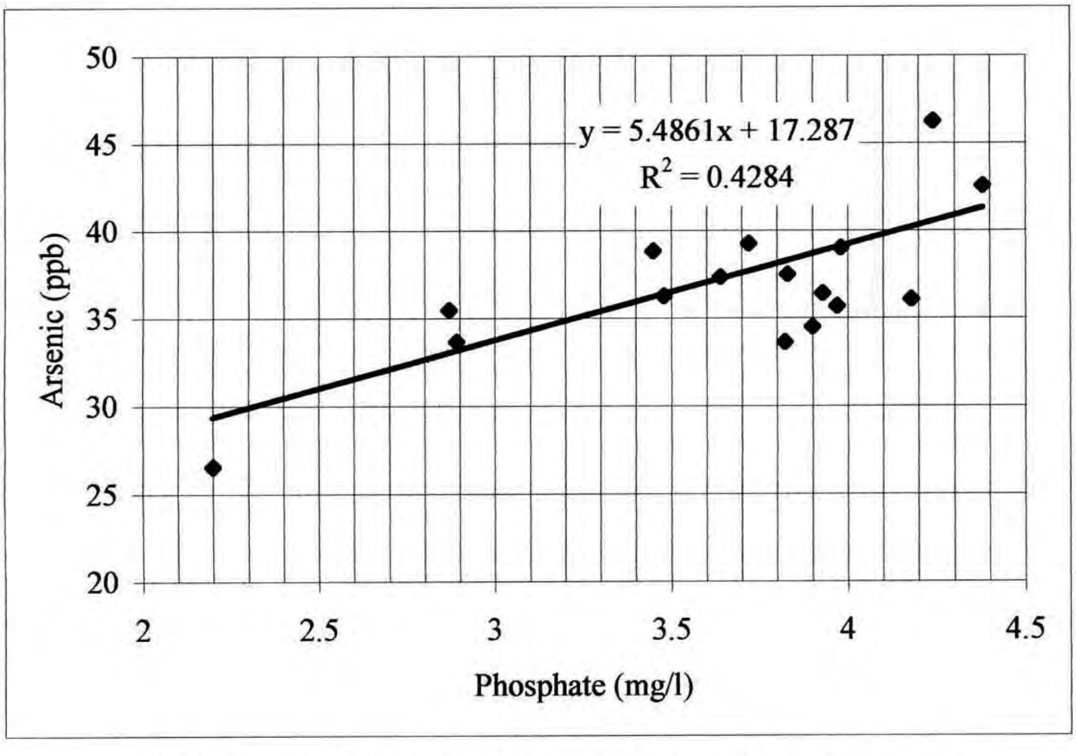


FIG. 6.4 Arsenic Leaching and Residual Phosphate concentration

6.3.4 CORRELATION BETWEEN ARSENIC LEACHING AND RESIDUAL NITRATE

10 mg/l of nitrate was used as extraction fluid media. From residual concentration of nitrate it is seen that leaching of arsenic decreases with the increase of residual nitrate ion concentration. As seen from Fig. 6.5 that arsenic leachate concentration shows an opposite pattern to residual nitrate concentration as leaching continues. Thus it can be concluded that As leachate concentration decrease with increase of residual NO_3^- concentration. It is also seen that residual nitrate ion concentration is lower than that of input concentration of nitrate ion.

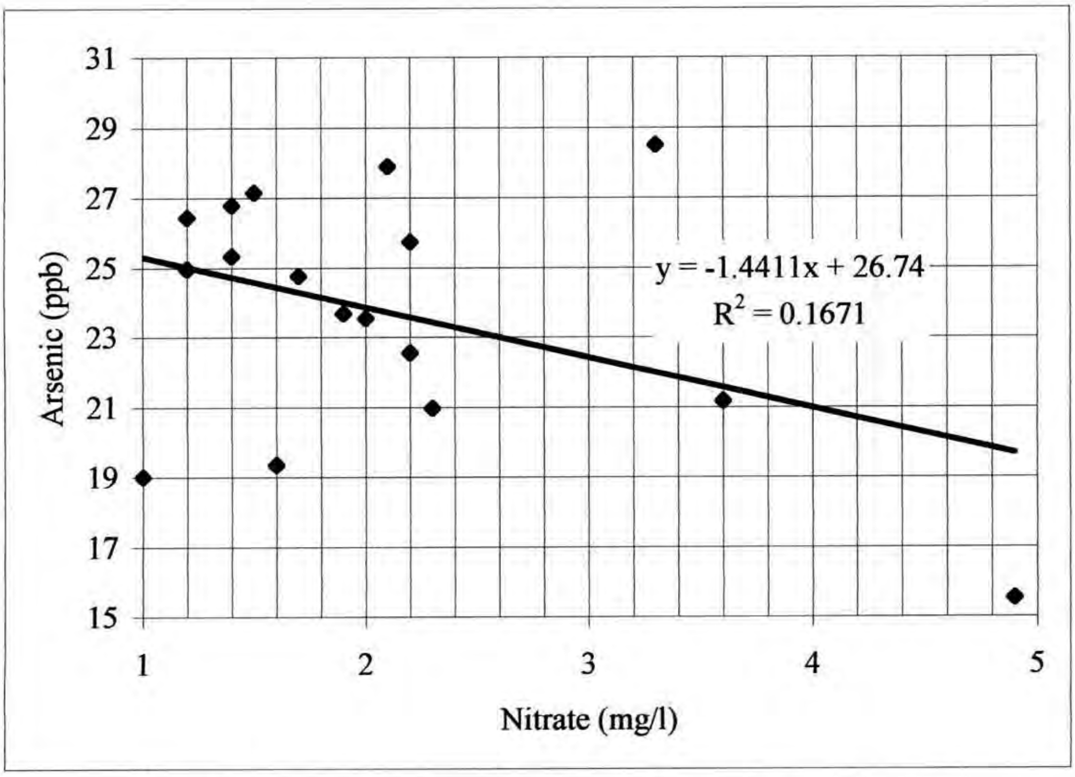


FIG. 6.5 Arsenic Leaching and Residual Nitrate concentration

6.3.5 CORRELATION BETWEEN ARSENIC LEACHING AND RESIDUAL SULPHATE

400 mg/l of sulphate was used as extraction fluid media. Results from Fig 6.6 indicate that arsenic leachate concentration is independent of residual sulphate concentration as arsenic leachate concentrations vary negligible in proportion with

variation of residual sulphate concentration. Thus, it may be concluded that nitrate ion has poor ability to leach arsenic from arsenic laden waste. Fig 6.6 further indicates that residual sulphate concentration is higher than that of input concentration indicating presence of sulphate bearing complexes in the sludge.

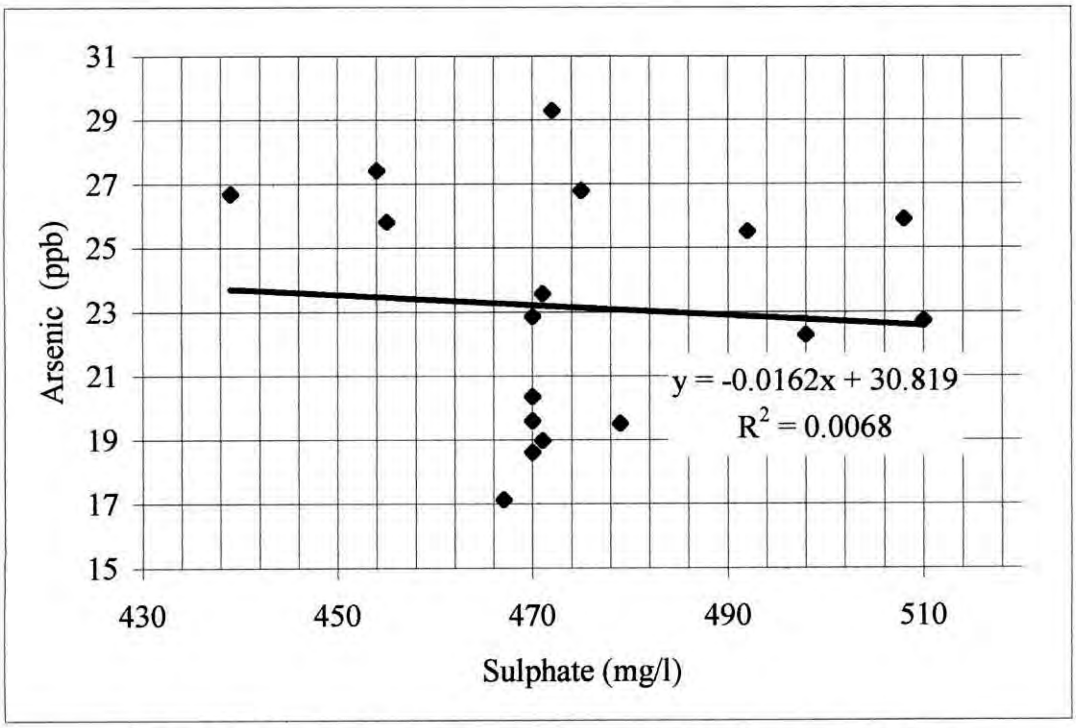


FIG. 6.6 Arsenic Leaching and Residual Sulphate concentration

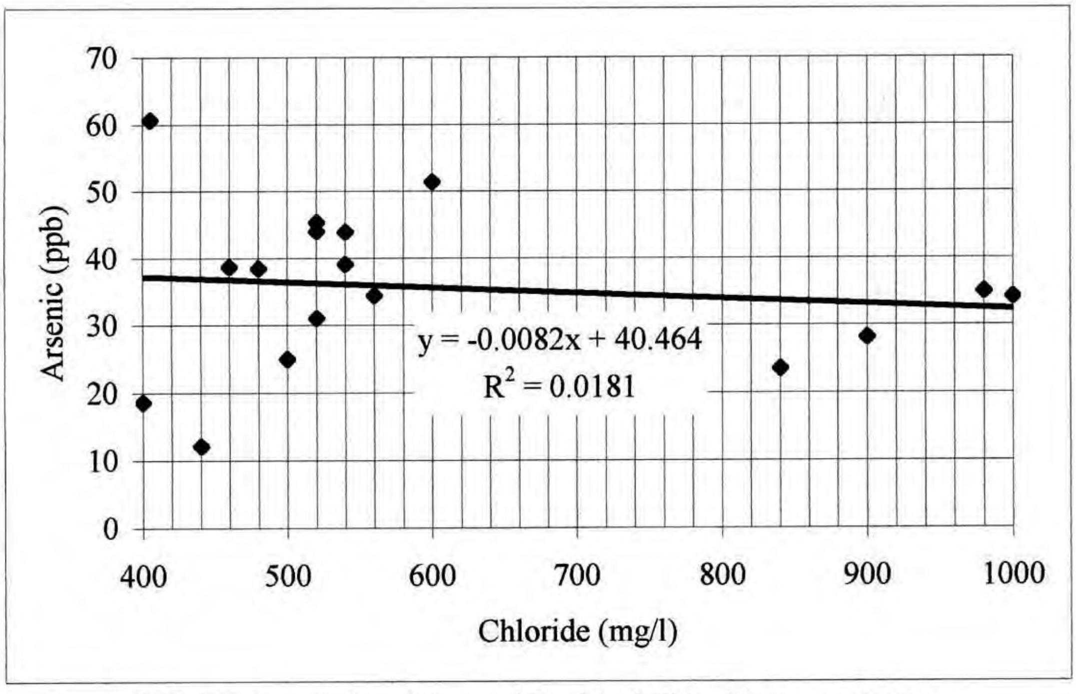


FIG. 6.7 Arsenic Leaching and Residual Chloride concentration

6.3.6 CORRELATION BETWEEN ARSENIC LEACHING AND RESIDUAL CHLORIDE

Total 500 mg/l chloride was used in extraction fluid media. Results from Fig 6.7 indicate that leaching of arsenic is independent of chloride content as the variation of As leachate concentration is very low corresponding to increase in residual chloride concentration. Thus it can be concluded that chloride ion has poor ability to leach As from arsenic laden waste. It further shows that residual concentration of chloride higher than that of input concentration indicating increased chloride salt concentration in the sludge.

6.4 SUMMARY OF THE STUDY

TCLP may not be suitable for assessment of long-term leaching of arsenic from arsenic-rich waste, because such leaching may be kinetically restricted. Column is aimed at carrying out long term leaching from arsenic laden waste. Hence column leaching may be kinetically directed. Column leaching takes longer time than that of TCLP, but it provides better performance in assessing leaching concentration from arsenic laden waste. From results of Column leaching it can be concluded that column leaching is more effective and acceptable in term of assessing leaching concentration from arsenic laden waste. It is also seen that individual anion causes higher leaching than that of combined effect of anions in a fluid media. Results of Arsenic leachate concentration from TCLP and Column leaching indicate that leachate concentration from Column leaching reflects a comprehensive and better result than that of TCLP. In case of TCLP leachate concentrations from both sludge and burnt bricks were considered to be well below USEPA regulatory value, whereas in case of Column leaching it is seen that leachate concentration from sludge crossed USEPA regulatory value onward 6th day of leaching. However, in both TCLP and Column leaching technique phosphate anion extraction fluid shows to cause higher leachate concentration than other types of extraction fluid media.

Higher leaching concentration from phosphate anion extraction fluid indicates affinity of phosphate ion for arsenic. Thus use of artificial fertilizer for higher production of crops might lead to increased leaching of arsenic laden waste being disposed off on surface. From residual concentration of nitrate it is seen that leaching of arsenic decreases with the increase of residual nitrate ion concentration. Thus it can be concluded that As leachate concentration decrease with increase of residual NO_3^- concentration. Arsenic leachate concentration is independent of residual sulphate concentration as arsenic leachate concentrations vary negligible in proportion with variation of residual sulphate concentration. Thus, it may be concluded that nitrate ion has poor ability to leach arsenic from arsenic laden waste. As leachate concentration is very low corresponding to increase in residual chloride concentration. Thus it can be concluded that chloride ion has poor ability to leach As from arsenic laden waste. Initial high concentration of arsenic from bricks sample and thereafter sharp fall with leaching period indicates that residual unbound arsenic in the burnt sample release as early as possible and thereafter it fall sharply as arsenic co precipitates with naturally occurring iron in the water. Further iron is oxidised to form metal oxides while experiencing heavy temperature during heating of bricks sample at high temperature.

CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The research work has demonstrated a feasible way of using arsenic and iron sludge as a clay substitute to produce quality bricks. Different measurements of both clay-sludge mixture and bricks were carried out to evaluate the factors that could affect brick quality. Major conclusions are derived from the analysis of result and discussions are summarised below:

Arsenic content in the raw sludge was found to be almost double than that present in stabilized sludge. However, in case of leaching it was seen that leaching of arsenic was more in case of stabilized sludge. TCLP test of sludge indicated that leaching of arsenic from sludge is more than that of burnt bricks. Though TCLP result of both sludge and burnt bricks don't indicate it, as hazardous waste but leaching values are far more than drinking water arsenic concentration. Increasing the firing temperature resulted in decrease in leaching of arsenic. However, leachate concentration at varying temperature indicates it to be independent of temperature and mix proportion down to 15% since TCLP simulate the leaching actions that occur in landfills. Arsenic co precipitate with iron during water treatment and process of cementation occurs between these two substances. This can be attributed to the metal form (Fe) in the sludge that has been converted to oxides during heating at high temperature.

Leachate concentration from column leaching test indicates higher leachate concentration of brick sample at initial stage, indicating leaching of residual free arsenic content present in bricks. However, with progress of duration leachate concentration of bricks decrease sharply well below original sludge leachate concentration and maintain a steady state indicating very meagre leaching rate with respect to original sludge leachate. Apart from bricks sample leachate concentration of sludge in different media progress in a bandwidth. Within the bandwidth phosphate and chloride anion bound indicate prominence in leachate concentration.

From fluid dripping rate and leachate concentration it is observed that leachate and dripping volume is inversely proportional indicating that leaching is dependent on contact period. A correlation may be drawn between TCLP and Column Leaching, stating that leachate concentration in case of column leaching is more than leachate concentration from TCLP.

Arsenic content in various mixes proportions with varying environmental conditions represent dissimilar value. The proportionate decrease or increase of arsenic content in raw sludge-clay mix and after burning shows remarkable difference. On burning a handsome amount of decrease in arsenic content is seen. On the other hand arsenic content variation is bare minimum with variation of mix proportion in case of leached extract of arsenic from sludge. However, arsenic content in residual sample after carrying out TCLP reflects similar result like arsenic content of burnt sample. It is further observed that arsenic content after burning is total sum of leached arsenic and residual arsenic in the sludge after. Burning of mixes of varying proportions enhances biomethylation of arsenic. Burning of arsenic sludge is an aid to the restriction of arsenic mobility in geochemical environment.

The results of compressive strength tests on the bricks indicate that the strength is greatly dependent on the amount of sludge in the brick and the firing temperature. The optimum amount of sludge that could be mixed with clay to produce good bonding of bricks was 15% by weight firing at 1000^0C. With up to 25% sludge added to the bricks and fired at 1050^0C, the strength can be as high as that of normal clay bricks. The compressive strength of bricks made from sludge–clay mixtures all meets the BDS 208 (1980) brick standard.

Increasing the amount of sludge in the clay, the SSA of that corresponding mixture increases proportionally. As a result, the overall particle fineness and water requirement for mixing increase with increasing percentage of sludge in the mixture. Increasing the amount of sludge added in the mixture results in a decrease in its plastic behaviour.

The brick manufactured did not show any deformation or uneven surfaces occurring at all firing temperatures with OMC applied in the mixtures of varying proportions. Increasing the firing temperature and decreasing the amount of sludge in the brick resulted in a decrease in water absorption.

In order to yield a good quality brick, the proportion of sludge and the firing temperature are the two key factors controlling the shrinkage in the firing process. Firing shrinkage increase rapidly up to 15% mix proportion. However, a linear relationship between the shrinkage and the sludge proportion was observed for 15 to 50% sludge added. A good quality brick can be produced under the following conditions fewer than 15% sludge used and fired at 1000^0C.

Increasing the percentage off sludge resulted in an increase in brick weight loss. The bricks made for this study all meet the criterion of 15% weight loss on ignition for a normal clay brick. The bulk density of brick was seen to be inversely proportional to the quantity of sludge added in the mixture. This finding was closely related to the quantity of water absorbed in the brick. When bricks absorb more water, it exhibits a large pore size than one with less water absorption. As a result bulk density becomes smaller.

7.2 RECOMMENDATIONS

The major focus of this study was to assess the effects of using arsenic-iron sludge in brick making. In all, the recommended proportion of sludge in brick making is 15 to 25% and fired at 1000 to 1050^0C to produce a good quality brick. It was revealed that addition of sludge up to 25% retain the original characteristics of normal clay bricks. Further, leaching of arsenic is largely reduced when sludge mix is burnt at high temperature in the brick making process. Major recommendations for continuation of the present work in the future is summarised below:

Bricks out of arsenic-iron sludge and clay mix were prepared in the laboratory. For the purpose of research, temperature manage and quality control initial drying of green bricks were carried in the oven at 105^0C and actual burning was conducted in Carbolite heavy duty oven at controlled temperatures. Hence, an effort may be taken in future to prepare bricks in the field (brickfield) with a view to assess its quality with the prepared brick in the laboratory. Depending on this assessment commercial production of bricks out of arsenic-iron sludge and clay mix may be recommended with necessary modifications and suggestions.

TCLP of burnt sludge-clay mix of varying proportion and firing temperature was carried out at fixed pH as indicated in the standard procedure. Hence, TCLP may be done in varying pH since adsorption and desorption of arsenic in the environment varies widely with change of pH.

Mass balance analysis was carried out for arsenic in TCLP extracts. Same analysis can be undertaken in terms of arsenic extracts in column leaching in future, since column leaching reflects a better output than that of TCLP. An analysis out of these two mass balance analysis may also be carried with a view to draw a correlation between mass balance analysis with TCLP and column leaching.

Column leaching was done with fixed surface area of passing media. Future study may be carried out on the same model with varying surface area by altering diameter of burette.

Column leaching apparatus was prepared by improvised means. During experiment it was observed that dripping of extraction fluid through media varied widely and affected arsenic concentration in the leached extract. Hence, an effort may be taken in prospect to calibrate column-leaching apparatus and thus recommend a standard column leaching apparatus.

Effect of anion of different parameter on arsenic leaching and treatment reflects reverse impact. Thus, in future, a study may be undertaken to assess impacts of various anion bound on varying arsenic treatment and leaching procedure with a view to draw a correlation between these two effects.

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APPENDIX A

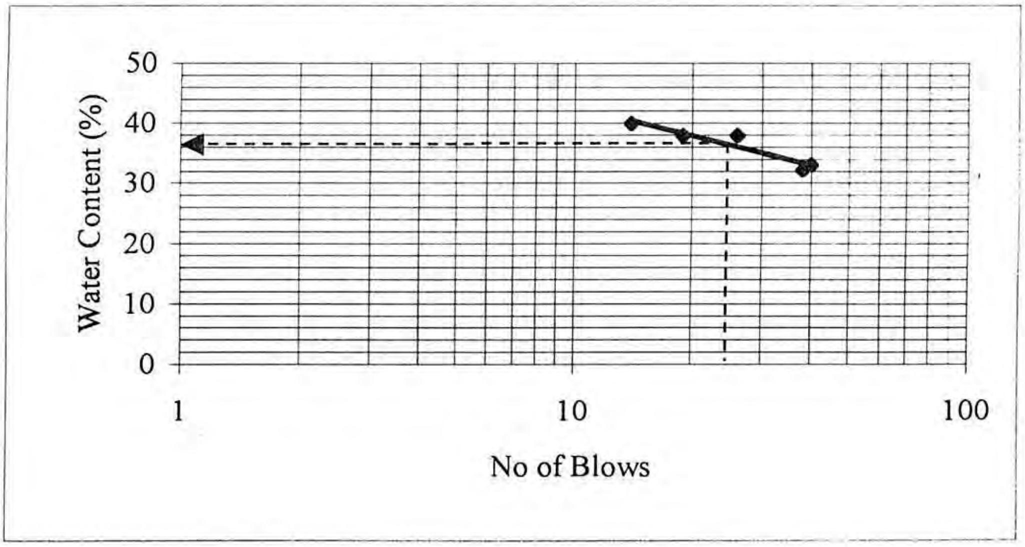
Geotechnical Engineering Laboratory
Department of Civil Engineering

Atterberg Limit Test

Soil Sample: 0% Sludge	Test No:
Tested by: 100104502	Date:

Liquid Limit					
No of Blows	14	19	26	38	40
Container No	757	905	55	19	403
Wt of Container, gm	7	10.6	7.3	7	6.7
Wt of Container + Wet Soil	41.7	36.7	38.4	39.8	37.9
Wt of Container + Dry Soil	31.8	29.52	29.85	31.81	30.15
Wt of Water, W1 in gm	9.9	7.18	8.55	7.99	7.75
Wt of Dry Soil, W2 in gm '	24.8	18.92	22.55	24.81	23.45
Water Content, W in %	39.92	37.949	37.916	32.204756	33.049
Plastic Limit					
Container No	129	807	743		
Wt of Container, gm	7.2	6.9	7.5		
Wt of Container + Wet Soil	17.83	17.72	18.12		
Wt of Container + Dry Soil	16.21	15.9	16.6		
Wt of Water, W1 in gm	1.62	1.82	1.52		
Wt of Dry Soil, W2 in gm '	9.01	9	9.1		
Water Content, W in %	17.98	20.222	16.703		

Liquid Limit:	36.26
Plastic Limit:	18.3
Plasticity Index:	17.96



Geotechnical Engineering Laboratory
Department of Civil Engineering

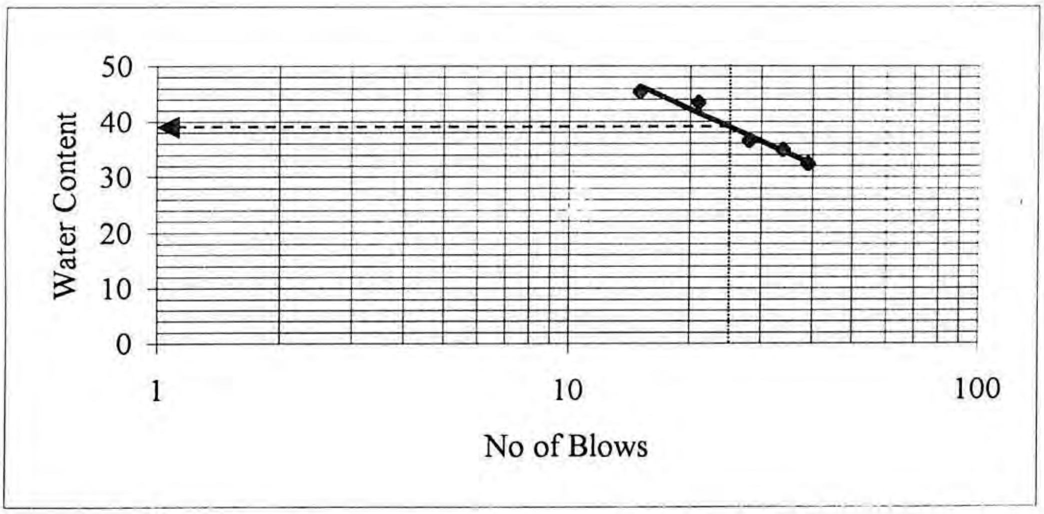
Atterberg Limit Test

Soil Sample: 5% Sludge	Test No:
Tested by: 100104502	Date:

Liquid Limit					
No of Blows	15	21	28	34	39
Container No	757	905	55	19	403
Wt of Container, gm	7	10.6	7.3	7	6.7
Wt of Container + Wet Soil	43.2	40.18	40.81	41.81	39.56
Wt of Container + Dry Soil	31.9	31.22	31.85	32.81	31.54
Wt of Water, W1 in gm	11.3	8.96	8.96	9	8.02
Wt of Dry Soil, W2 in gm '	24.9	20.62	24.55	25.81	24.84
Water Content, W in %	45.382	43.453	36.497	34.870205	32.287

Plastic Limit					
Container No	129	807	743		
Wt of Container, gm	7.2	6.9	7.5		
Wt of Container + Wet Soil	17.41	18.91	18.7		
Wt of Container + Dry Soil	15.5	16.7	16.6		
Wt of Water, W1 in gm	1.91	2.21	2.1		
Wt of Dry Soil, W2 in gm '	8.3	9.8	9.1		
Water Content, W in %	23.012	22.551	23.077		

Liquid Limit:	39.54
Plastic Limit:	22.88
Plasticity Index:	16.66



Geotechnical Engineering Laboratory
Department of Civil Engineering

Atterberg Limit Test

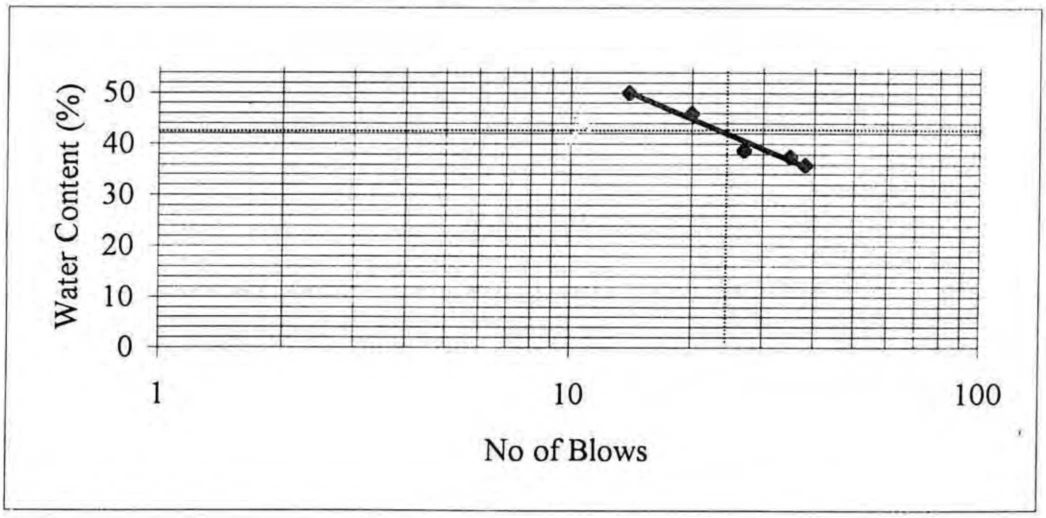
Soil Sample: 15 % Sludge
Tested by: 100104502

Test No:
Date:

Liquid Limit					
No of Blows	14	20	27	35	38
Container No	757	905	55	19	403
Wt of Container, gm	7	10.6	7.3	7	6.7
Wt of Container + Wet Soil	42.85	40.68	40.81	41.1	39.36
Wt of Container + Dry Soil	30.9	31.22	31.45	31.81	30.74
Wt of Water, W1 in gm	11.95	9.46	9.36	9.29	8.62
Wt of Dry Soil, W2 in gm	23.9	20.62	24.15	24.81	24.04
Water Content, W in %	50	45.878	38.758	37.444579	35.857

Plastic Limit					
Container No	129	807	743		
Wt of Container, gm	7.2	6.9	7.5		
Wt of Container + Wet Soil	17.81	18.9	18.55		
Wt of Container + Dry Soil	15.55	16.39	16.16		
Wt of Water, W1 in gm	2.26	2.51	2.39		
Wt of Dry Soil, W2 in gm '	8.35	9.49	8.66		
Water Content, W in %	27.066	26.449	27.598		

Liquid Limit:	42.25
Plastic Limit:	27.038
Plasticity Index:	15.212



Geotechnical Engineering Laboratory
Department of Civil Engineering

Atterberg Limit Test

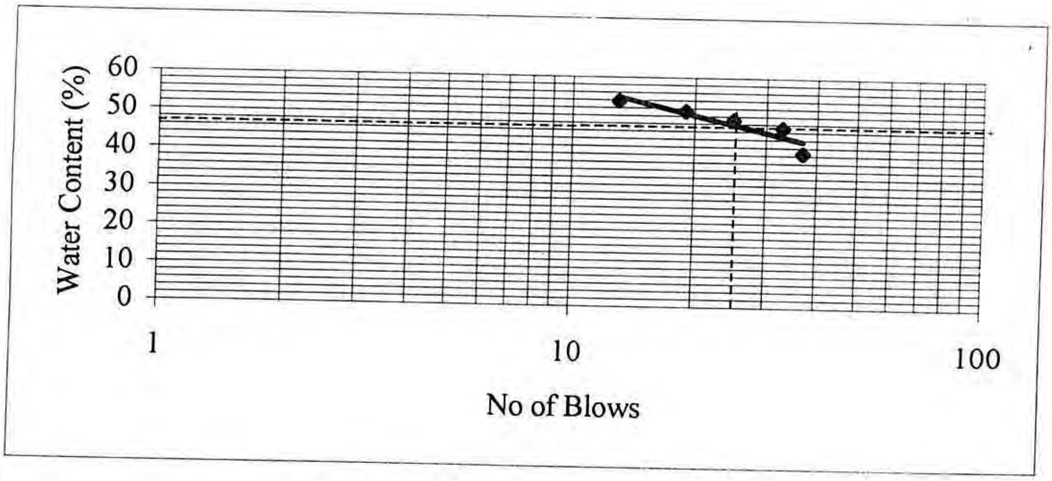
Soil Sample: 25% Sludge
Tested by: 100104502

Test No:
Date:

Liquid Limit					
No of Blows	13	19	25	33	37
Container No	757	905	55	19	403
Wt of Container, gm	7	10.6	7.3	7	6.7
Wt of Container + Wet Soil	43.71	41.78	42.82	42.12	40.46
Wt of Container + Dry Soil	30.9	31.22	31.15	30.91	30.74
Wt of Water, W1 in gm	12.81	10.56	11.67	11.21	9.72
Wt of Dry Soil, W2 in gm	23.9	20.62	23.85	23.91	24.04
Water Content, W in %	53.598	51.212	48.931	46.884149	40.433

Plastic Limit					
Container No	129	807	743		
Wt of Container, gm	7.2	6.9	7.5		
Wt of Container + Wet Soil	18.3	18.89	18.55		
Wt of Container + Dry Soil	15.55	15.69	15.71		
Wt of Water, W1 in gm	2.75	3.2	2.84		
Wt of Dry Soil, W2 in gm '	8.35	8.79	8.21		
Water Content, W in %	32.934	36.405	34.592		

Liquid Limit:	47.08
Plastic Limit:	34.644
Plasticity Index:	12.436



Geotechnical Engineering Laboratory
Department of Civil Engineering

Atterberg Limit Test

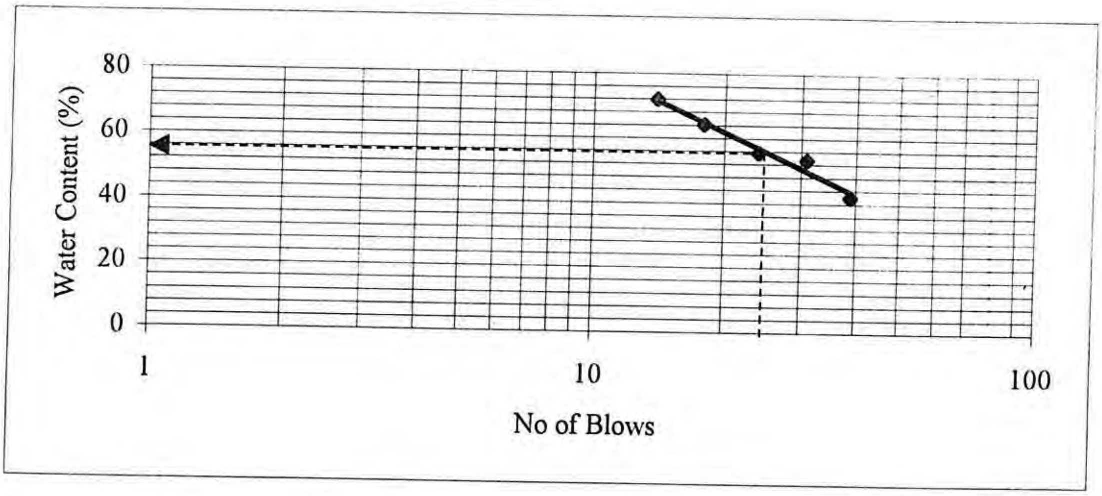
Soil Sample: 50% Sludge
Tested by: 100104502

Test No:
Date:

Liquid Limit					
No of Blows	14	18	24	31	39
Container No	757	905	55	19	403
Wt of Container, gm	7	10.6	7.3	7	6.7
Wt of Container + Wet Soil	44.71	43.78	42.82	42.12	40.53
Wt of Container + Dry Soil	28.94	30.82	30.15	29.93	30.54
Wt of Water, W1 in gm	15.77	12.96	12.67	12.19	9.99
Wt of Dry Soil, W2 in gm	21.94	20.22	22.85	22.93	23.84
Water Content, W in %	71.8778	64.095	55.4486	53.1618	41.9044

Plastic Limit					
Container No	129	807	743		
Wt of Container, gm	7.2	6.9	7.5		
Wt of Container + Wet Soil	19.23	19.84	19.5		
Wt of Container + Dry Soil	15.51	15.89	15.83		
Wt of Water, W1 in gm	3.72	3.95	3.67		
Wt of Dry Soil, W2 in gm	8.31	8.99	8.33		
Water Content, W in %	44.7653	43.9377	44.0576		

Liquid Limit:	56.08
Plastic Limit:	44.2536
Plasticity Index:	11.8264



APPENDIX B

Department of Civil Engineering

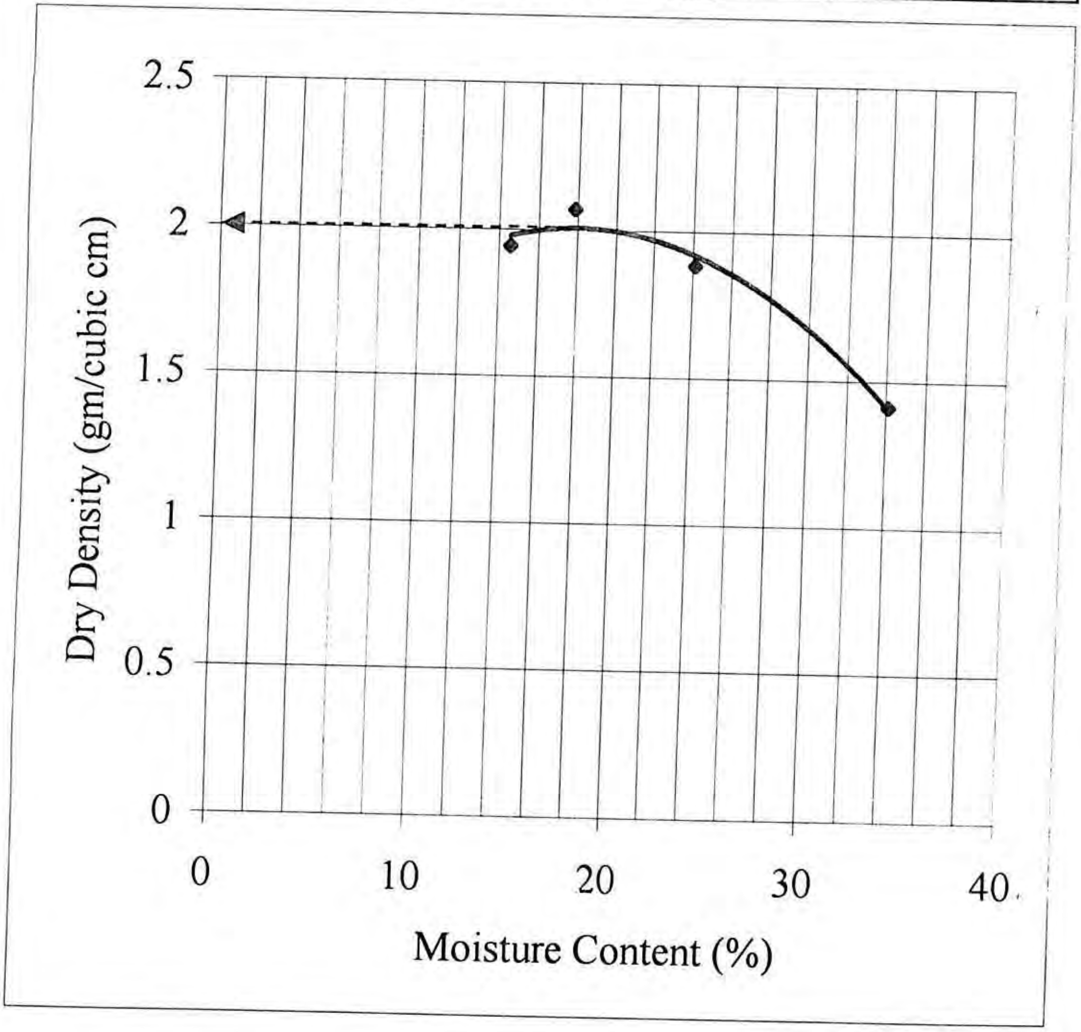
Geotechnical Engineering Laboratory

Compaction test

Date:

Sample No: 0% Sludge **Tested By:** 100104502

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)	MC %	Avg MC %	Wt of Mold (gm)	Wt of Mold +Compacted Soil (gm)	Wt of Compacted Soil (gm)	Weight Density gm/cm3	Dry Density gm/cm3
1	809	6.5	23.5	21.32	14.82	2.18	14.71	14.6	4230	6295	2065	2.228	1.944
2	138	7.2	27.8	25.19	17.99	2.61	14.51						
3	907	7.5	29.6	26.38	18.88	3.22	17.06	17.9	4230	6493	2263	2.442	2.072
4	141	7.3	29.18	25.73	18.43	3.45	18.72						
5	18	7.4	33.15	28.19	20.79	4.96	23.86	24.1	4230	6398	2168	2.34	1.885
6	746	7.7	33.85	28.72	21.02	5.13	24.39						
7	810	7.3	49.9	39.17	31.87	10.7	33.67	34.1	4230	5985	1755	1.894	1.412
8	722	7.1	47.1	36.82	29.72	10.3	34.59						



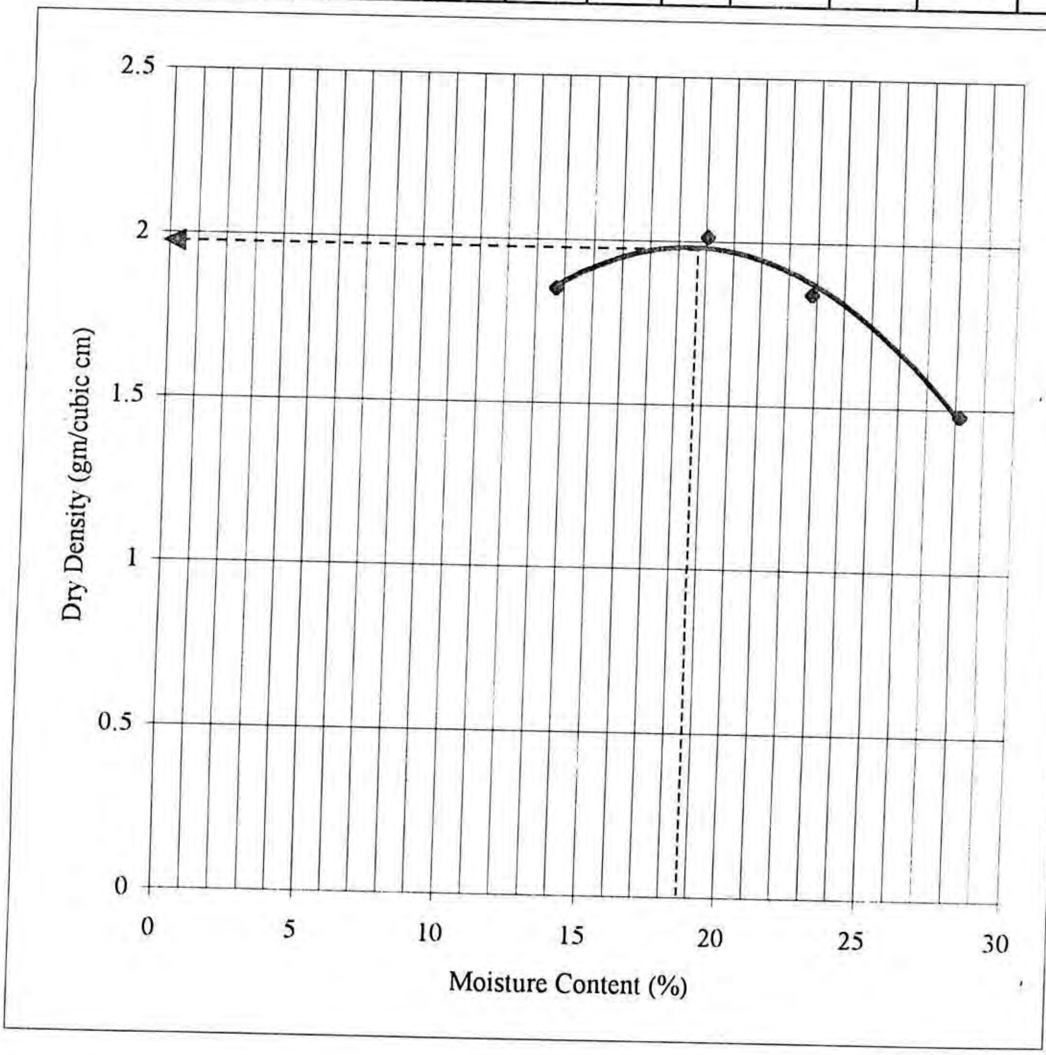
Department of Civil Engineering

Geotechnical Engineering Laboratory

Compation Test

Date: **Sample No:** 5% Sludge **Tested By:** 100104502

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)	MC %	Avg MC %	Wt of Mold (gm)	Wt of Mold +Compacted Soil (gm)	Wt of Compacted Soil (gm)	Weight Density gm/cm3	Dry Density gm/cm3
1	809	6.5	22.5	20.6	14.1	1.9	13.48	13.7	4230	6180	1950	2.1043	1.8501
2	138	7.2	30.8	27.9	20.7	2.9	14.01						
3	907	7.5	30.6	26.8	19.3	3.8	19.69	19.1	4230	6453	2223	2.3989	2.015
4	141	7.3	29.8	26.3	19	3.5	18.42						
5	18	7.4	32.5	27.9	20.5	4.6	22.44	22.9	4230	6328	2098	2.264	1.8429
6	746	7.7	32.6	27.9	20.2	4.7	23.27						
7	810	7.3	48.9	39.7	32.4	9.2	28.4	28.2	4230	5985	1755	1.8939	1.4776
8	722	7.1	45.1	36.8	29.7	8.3	27.95						



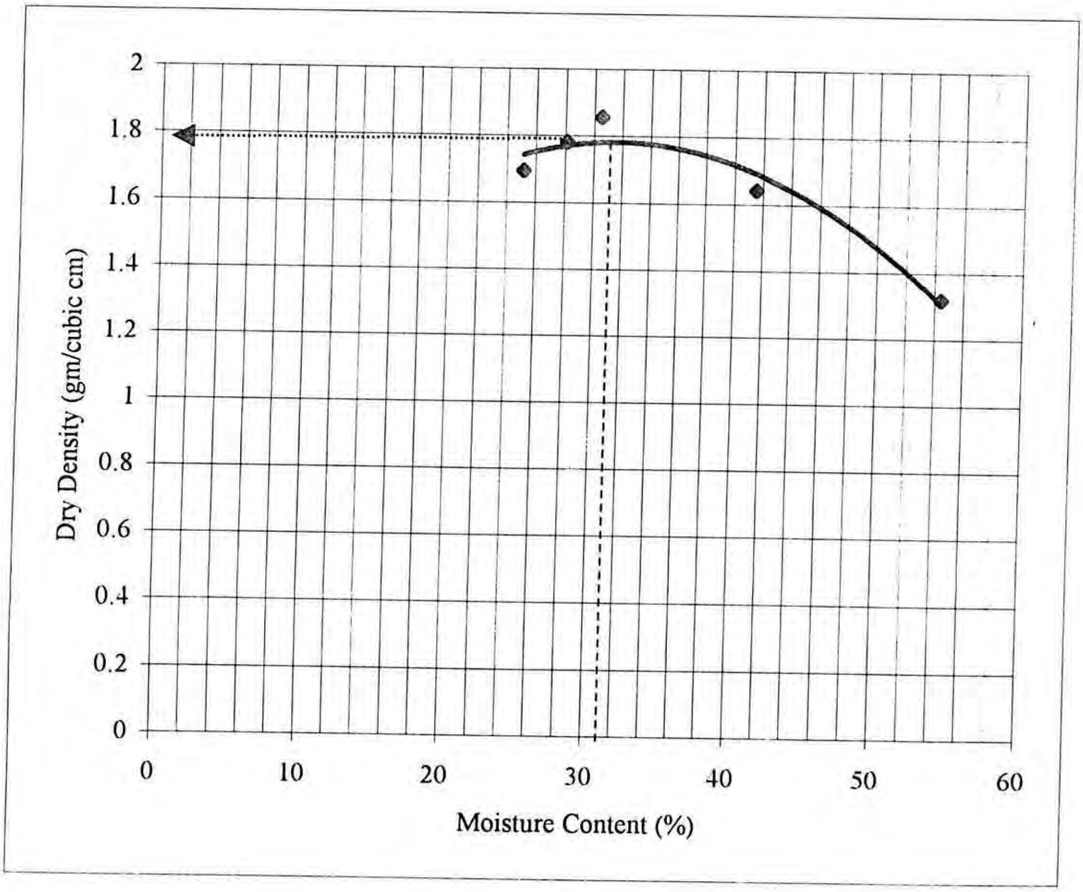
Department of Civil Engineering

Geotechnical Engineering Laboratory

Compaction Test

Date: **Sample No:** 15% Sludge **Tested By:** 100104502

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)	MC %	Avg MC %	Wt of Mold (gm)	Wt of Mold +Compacted Soil (gm)	Wt of Compacted Soil (gm)	Weight Density gm/cm3	Dry Density gm/cm3
1	809	6.5	32.5	27.22	20.72	5.28	25.5	25.2	4230	6195	1965	2.1205	1.694
2	138	7.2	31.8	26.9	19.7	4.9	24.9						
3	907	7.5	34.6	28.78	21.28	5.82	27.3	28.1	4230	6345	2115	2.2824	1.7811
4	141	7.3	35.2	28.93	21.63	6.26	28.9						
5	18	7.4	32.8	26.69	19.29	6.06	31.4	30.5	4230	6474	2244	2.4216	1.8551
6	746	7.7	43.9	35.59	27.89	8.27	29.7						
7	810	7.3	44.7	33.7	26.4	11	41.7	41.5	4230	6385	2155	2.3255	1.643
8	722	7.1	49.1	36.8	29.7	12.3	41.4						
9	805	7.1	55.9	38.62	31.52	17.3	54.8	54.5	4230	6119	1889	2.0385	1.3197
10	7	7.1	52.4	36.47	29.37	15.9	54.1						



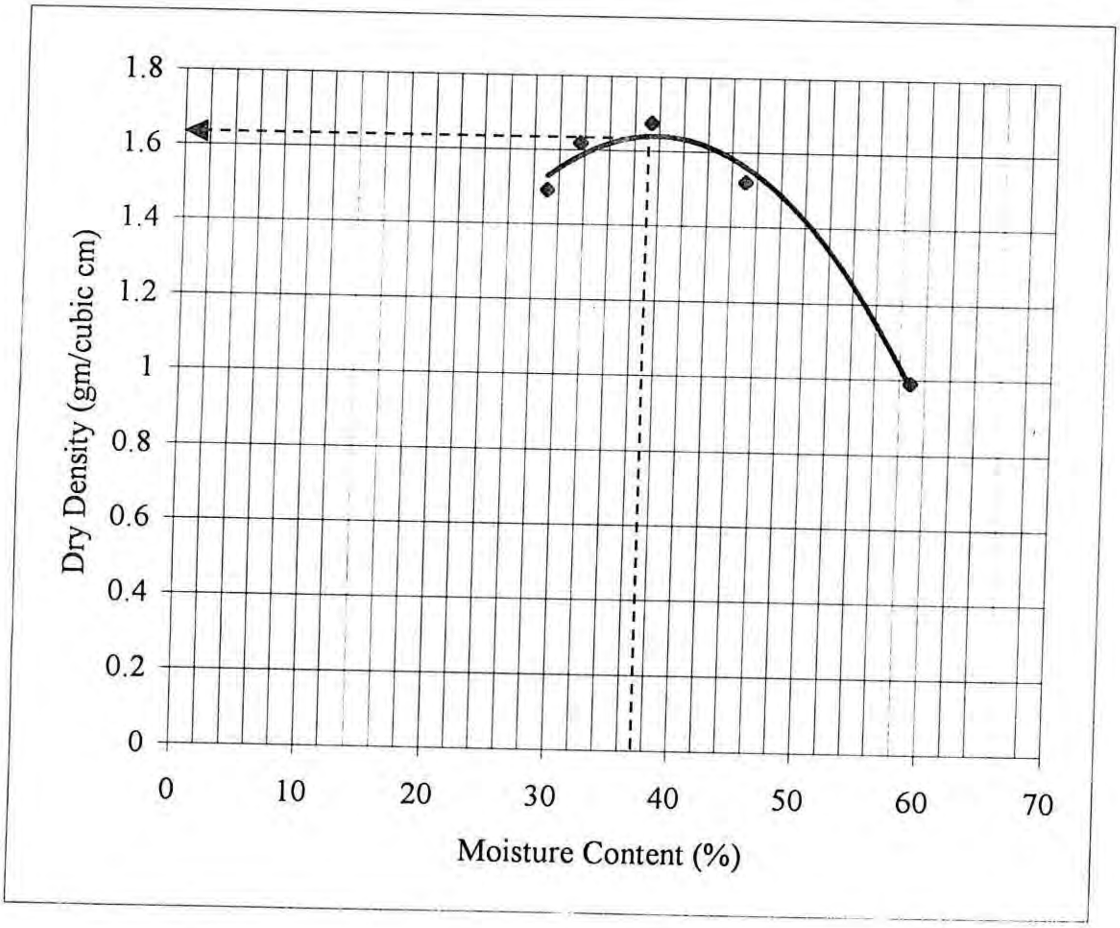
Department of Civil Engineering

Geotechnical Engineering Laboratory

Compaction Test

Date: **Sample No:** 25% Sludge **Tested By:** 100104502

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)	MC %	Avg MC %	Wt of Mold (gm)	Wt of Mold +Compacted Soil (gm)	Wt of Compacted Soil (gm)	Weight Density gm/cm3	Dry Density gm/cm3
1	809	6.5	31.65	25.9	19.4	5.73	29.51	29.15	4230	6015	1785	1.9263	1.4915
2	138	7.2	30.37	25.2	18	5.18	28.79						
3	907	7.5	35.6	28.8	21.3	6.81	31.99	31.7	4230	6205	1975	2.1313	1.6183
4	141	7.3	35.79	29	21.7	6.81	31.41						
5	18	7.4	33.75	26.7	19.3	7.06	36.6	37.4	4230	6364	2134	2.3029	1.6761
6	746	7.7	44.86	34.6	26.9	10.3	38.19						
7	810	7.3	45.7	33.7	26.4	12	45.34	45.16	4230	6275	2045	2.2068	1.5202
8	722	7.1	48.71	35.8	28.7	12.9	44.98						
9	805	7.1	56.91	38.6	31.5	18.3	57.93	58.89	4230	5689	1459	1.5745	0.9909
10	7	7.1	54.37	36.7	29.6	17.7	59.86						



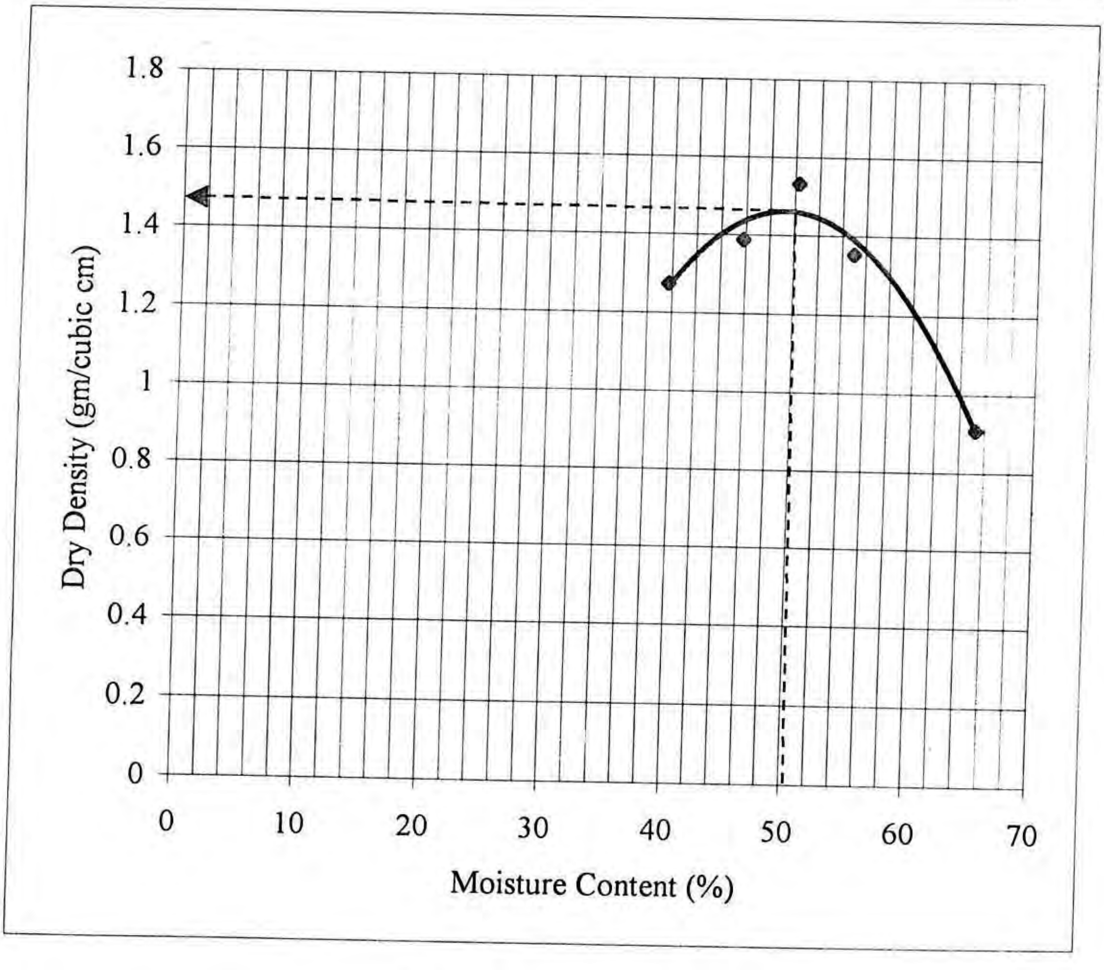
Department of Civil Engineering

Geotechnical Engineering Laboratory

Compaction Test

Date: **Sample No:** 50% Sludge **Tested By:** 100104502

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)	MC %	Avg MC %	Wt of Mold (gm)	Wt of Mold +Compacted Soil (gm)	Wt of Compacted Soil (gm)	Weight Density gm/cm3	Dry Density gm/cm3
1	809	6.5	33.75	25.92	19.42	7.83	40.32	39.73	4230	5879	1649	1.779	1.274
2	138	7.2	32.37	25.29	18.09	7.08	39.14						
3	907	7.5	38.6	28.74	21.24	9.86	46.42	45.84	4230	6105	1875	2.023	1.387
4	141	7.3	38.79	28.98	21.68	9.81	45.25						
5	18	7.4	43.75	31.69	24.29	12.06	49.65	50.31	4230	6364	2134	2.303	1.532
6	746	7.7	47.86	34.3	26.6	13.56	50.98						
7	810	7.3	52.7	36.75	29.45	15.95	54.16	55.03	4230	6175	1945	2.099	1.354
8	722	7.1	55.71	38.28	31.18	17.43	55.9						
9	805	7.1	55.7	36.62	29.52	19.08	64.63	65.34	4230	5621	1391	1.501	0.908
10	7	7.1	58.71	38.18	31.08	20.53	66.06						



APPENDIX C

TOXICITY CHARACTERISTICS LEACHING PROCEDURE (TCLP)

1. INTRODUCTION

The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphase wastes. If a total analysis of the waste demonstrates that individual analytes are not present in the waste or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run. If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyse the remaining fractions of the extract. If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the zero headspace extractor (ZHE) is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level (Badruzzaman, 2003).

2. SUMMARY OF METHOD

For liquid wastes (those containing less than 0.5% dry solid material) the waste after filtration through a 0.6 to 0.8 μm glass fibre filter is defined as the TCLP extract. For wastes containing greater than or equal to 0.5% solids, the liquid if any is separated from the solid phase and stored for later analysis; the particle size of the of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fibre filter (Badruzzaman, 2003). If compatible the initial liquid phase of the waste is added to the liquid extract and these are analysed together. If incompatible, the liquids are analysed separately and the results are mathematically combined to yield a volume weighted average concentration.

3. REAGENTS AND ACIDS

Reagent water is defined as water in which an interferant is not observed at or above the method's detection limit of the analytes of interest. For non-volatile extractions, ASTM Type II water or equivalent meets the determination of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods: (a) Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 gms of activated carbon, (b) A water purification system may also be used to generate reagent water for volatile extractions and (c) Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Reagent grade chemicals should be used in all tests. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Following acids are essential in conducting TCLP: (a) Hydrochloric acid (1N), HNO_3, made from ACS reagent grade; (b) Nitric acid (1N), NaOH, made from ACS reagent grade; (d) Glacial acetic acid CH_3CH_2COOH made from ACS reagent grade.

4. EXTRACTION FLUID

Extraction fluid type 1 is prepared by adding 5.7 ml glacial CH_3CH_2COOH to 500 ml of reagent water and 64.3 ml of 1N NaOH and diluted to a volume of 1 litre. When correctly prepared, the pH of this fluid should be 4.93 ± 0.05. Extraction fluid type 2 is prepared by diluting 5.7 ml glacial CH_3CH_2COOH with reagent water to a volume of 1 litre. When correctly prepared, the pH of this fluid should be 2.88±0.05. These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the mentioned specifications, the fluid should be discarded and fresh extraction fluid is prepared. TCLP extracts should be prepared for analysis and analysed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (Badruzzaman, 2003). Extracts should be preserved according to the guidance given in the individual analysis methods.

5. PRELIMINARY EVALUATION FOR TCLP

Preliminary TCLP evaluation is performed on a minimum 100b gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids, (2) determination of whether the waste contains insignificant solids and is therefore, its own extract after filtration, (3) determination of whether the solid portion of the waste requires particle size reduction and (4) determination of which of the two extraction fluids are to be used for the non-volatile TCLP extraction of the waste. Percent solid is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure. If the waste obviously yields no liquid when subjected to pressure filtration (i.e. is 100% solids) the extraction procedure should be followed without delay. If the sample is liquid or multiphase, liquid/solid separation to make a preliminary determination of percent solids is required. If the percent dry solid is less than 0.5%, the multiphase analysis method should be followed for non-volatile TCLP. Otherwise, if the percent dry solids ids greater than or equal to 0.5% and if the non-volatile TCLP is to be performed, particle size reduction analysis should be performed with a fresh portion of waste (Badruzzaman, 2003). Then the appropriate extraction liquid should be determined.

6. DETERMINATION OF APPROPRIATE EXTRACTION FLUID

If the solid content of the waste is greater than or equal to 0.5% and if the sample is extracted for non-volatile constituents, the appropriate fluid for non-volatile extraction should be determined. A small sub sample of solid phase of the waste is weighed and reduced (if necessary) to a particle size approximately 1 mm in diameter or less. Thereafter, 5.0 grams of solid phase of the waste is transferred to a 500 ml beaker. After adding 96.5 ml of reagent water to the beaker, it is to be covered with watch glass and be stirred vigorously for 5 minutes using a magnetic stirrer. Now the pH to be measured. If the pH of prepared extraction fluid is < 5.0, extraction fluid type 1 should be used. If the pH is > 5.0, 3.5 ml of 1N HCl to be added to reagent water. Thereafter, it is to be heated to 50^0 C for 10 minutes. Upon heating for 10 minutes the solution is to be cooled for about 10 minutes and pH to be recorded at this temperature. If the pH is < 5.0, extraction fluid type 1 to be used. If the pH is > 5.0, extraction fluid type 2 should be used.

7. TCLP FOR NON-VOLATILES

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample, whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganic, semi volatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analysis required. If the amount of extract generated by single TCLP extraction is not sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis. If the waste obviously yields no liquid when subjected to pressure filtration (i.e., is 100% solid, weigh out a sub-sample of the waste of minimum 100 gm) and extraction should be done directly as described later. Otherwise, if the sample is liquid or multiphase, liquid/solid separation is required. This involves the filtration. Following filtration, if required, the material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase (Badruzzaman, 2003). The filtrate should be weighed. The liquid phase may now be either analysed or stored at 4^0C until time of analysis.

If the waste contains <0.5% dry solids then it should be considered the TCLP extract and be preserved for analysis. However, if the percent of solids is >0.5% then it should be determined whether particle size reduction is necessary. If not then TCLP extraction procedure should be followed. Amount of extraction fluid needs to be added in the extraction vessel is determined by:

Weight of extraction fluid = [20x% solids x weight of the waste filtered]/100

This amount of appropriate extraction fluid is slowly added to the extractor vessel. It is then closed tightly, secured in rotary agitation device, and is rotated at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 ± 2^0C during the extraction period. It is important to note that as agitation continues, pressure may build up within the extractor bottle some types of waste (limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes and 1 hour) and vented into a hood. Following the 18 ± 2 hour extraction, the material in the extractor vessel should be separated into its component liquid and solid phase by filtering through a new glass fibre filter. If compatible (e.g., multiple phase will not result on combination), the filtered liquid resulting from the above step should be combined with the initial liquid phase of the waste obtained. This combined liquid is defined as the TCLP extract.

8. ANALYSIS OF TCLP EXTRACT

Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserved the extract for analysis. Metals aliquots must be acidified with nitric acid to pH < 2. If precipitation is observed upon addition nitric acid to a small aliquot of the extract, then the remaining portion of the extract shall be analysed as soon as possible (Badruzzaman, 2003). All other aliquots must be stored under refrigeration (4^0C) until analysed. The TCLP extract shall be prepared and analysed according to appropriate analytical methods. TCLP extracts to be analysed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts cannot be used to demonstrate that the waste is not hazardous. If the individual phases (to ± 0.5%), conduct the appropriate analyses and combine the results mathematically by using a simple volume - weighted average:

Final analyte concentration = $[V_1C_1 + V_2C_2]/[V_1+V_2]$

Where:

V_1= The volume of the first phase (L).
C_1= The concentration of the analyte of concentration in the first phase (mg/l).
V_2= The volume of the second phase (L).
C_2= The concentration of the analyte of concern in the second phase (mg/l).

APPENDIX D

BRICKS MANUFACTURING

1. GENERAL

A brick is an artificial kind of stone made of clay whose chief characteristics are a plasticity when wet and stone like hardness after being heated to high temperature (Aziz, 1995). Factors affecting quality of bricks are Chemical properties of the clay used, Preparation of the clay, Process of drying and Different degrees of burning. Building bricks are usually made of a mixture of clay and sand, which are mixed and moulded in various ways, after which they are dried and burnt. Clay for brick making must develop proper plasticity and be capable of drying rapidly without excessive shrinkage, warping and of being burnt to desired texture and strength (Tutunlu et al. 2001)

2. CONSTITUENTS OF BRICK CLAY AND THEIR FUNCTIONS

A good brick-clay should be such a mixture of pure clay and sand that when prepared with water, it can easily be moulded and dried without cracking or warping. It should also contain alumina, lime, iron oxide and magnesia. Chemical analysis of a good brick-clay indicates few chemicals as shown below:

Ser	Type of Chemicals	Fraction (%)
1.	Silica	55
2.	Alumina	30
3.	Iron Oxide	8
4.	Magnesia	5
5.	Lime	1
6.	Organic Matter	1

2.1 SILICA

Silica exists in all clays in a state of chemical combination with alumina forming silicate of alumina and some time exists in a free state when it is called flint or sand. The presence of sand prevents cracking, shrinking, and warping. The higher the proportion of sand, the more shapely and uniform in texture shall be the brick. But too much of sand makes the brick brittle and weak (Aziz, 1995).

2.2 ALUMINA (ALUMINIUM OXIDE) AND MAGNESIA (MAGNESIUM OXIDE)

This is the principal constituent of brick-clay. It imparts plasticity to clay, which is very essential for the purpose of moulding. It also imparts density. But the clay containing too much alumina should not be used because it causes brick to crack and wrap during burning (Aziz, 1995). Presence of magnesia in small quantity decreases shrinkage and gives yellow colour.

2.3 IRON OXIDE

The presence of iron oxide in clay enhances the impermeable and durable qualities. Iron and lime in small quantities give creamy colour to bricks. The colour of bricks is very much dependent upon the contents of iron and the colour ranges from light yellow to orange and red. The colour gradually deepens to red and then purple as the iron content goes up 8%. By adjusting the burning temperature, red colour due to presence of magnesium can be produced. Magnesia in presence of iron makes the brick yellow.

2.4 LIME

It reduces shrinkage of bricks during drying and enables the silica to melt in burning and thus binds the particles of brick together. In excess, however, it causes the brick to fuse too readily and the shape is lost. Lime should be present in a very finely divided state. Because, if it is present in the form of lumps it is very injurious to bricks since on burning it becomes quick lime and absorbs moisture-causing disintegration.

2.5 ALKALIES AND ORGANIC MATTER

A small quantity of organic matter assists in burning bricks. However, excess of organic matter is bad since it makes bricks porous if not completely burnt. Small quantities of alkalies lower the fusion point of clay.

3. HARMFUL CONSTITUENTS OF BRICKS

Few constituents make bricks unsuitable. These constituents include iron pyrites, alkalies, stone particles, vegetation, organic matter and lime. Effects of harmful constituents are enumerated below:

Ser	Type	Characteristics
1.	Iron Pyrites	Presence of pyrites cause crystallisation and disintegration of bricks on burning
2.	Alkalies	They are mainly the chlorides and sulphates of calcium, magnesium, sodium and potassium. They produce a dark greenish hue on the surface of bricks on drying. They cause the bricks to fuse, twist and warp during burning. Alkalies in bricks absorb moisture from air and on drying cause efflorescence.
3.	Stone Particles	Small particles of stones do not allow the clay to be mixed thoroughly and uniformly. These are harmful to the uniformity of brick texture. These make brick porous and weak.
4.	Vegetation and Organic Material	These make bricks porous and weak because vegetations and organic matter get burnt during the burning of bricks of bricks leaving small pores in them.
5.	Lime	Lime if present in excess causes the brick to fuse too readily and the shape is lost. Lime in the form of limestone and kankar nodules is very harmful and cause serious trouble to bricks. Because due to high heating limestone ($CaCO_3$) is converted into lime (CaO) and carbon dioxide (CO_2). On contact with water, lime gets hydrated and swells and causes the brick s to split and crumble to pieces. Limestone in the form of kankar nodules should not be present because it deteriorates the quality of a good brick.

4. BRICK BURNING

Bricks are burnt with a view to impart hardness and strength as well as to increase the density of it so that water absorption is reduced and thereby durability is increased. Great care and skill are required in burning bricks because under burnt bricks are soft and useless. Well-burnt bricks are hard, strong, compact and durable. Over burnt bricks again vitrify and hence not sound. During drying, free water contained in the clay gets removed due to evaporation, but the water, which incorporated with the clay in the form of water of crystallization, is removed only when the bricks are burnt. Bricks are burnt in clamps or kilns where the temperature is raised to about 2100^0F. At a temperature of about 1200^0F, the organic matter present in the bricks is oxidized and disappears. When the temperature rose to about 2100^0F, certain chemical changes take place in its constituent materials, giving new properties to the bricks. Particles of alumina and sand bind themselves together and that increases the density and strength of the bricks. Burning of alumina and sand grains produces fusible glass in small quantity. But when heated beyond 2100^0F, the fusible glass is formed in a much greater quantity and the bricks are said to be vitrified. Vitrification softens the bricks and they begin to loose their shape (Aziz, 1995).

5. CHARACTERISTICS OF GOOD BRICKS

(1) Bricks should be uniform in colour, size and shape.

(2) They should be sound and compact.

(3) They should be free from cracks and other flaws such as air bubbles, stone nodules, etc.

(4) They should not absorb more than 1/5 of their own weight of water when immerged in water for 24 hours (15 to 20% dry weight).

(5) The compressive strength of bricks should be I the range of 5000 to 8000 psi.

(6) The percentage of soluble salts (sulphates of calcium, magnesium, sodium and potassium) should not exceed 2.5% in burnt bricks, because the presence of excess soluble salts causes efflorescence.

(7) They should be neither over burnt nor under burnt.

(8) The weight should be generally 6 lbs per brick and the weight per cft should not be less than 125 lbs.

(9) They should have low thermal conductivity.

(10) They should be non-inflammable and incombustible.

(11) Bricks should not change in volume when wetted.

6. SIZE OF BRICKS

In Bangladesh, according to BDS-208 (1980) specification, each brick should measure 9.5 inch x 4.5 inch x 2.75 inch (Aziz, 1995). This is the standard size of bricks in Bangladesh. There are other sized bricks also. But this size is most economical. Because when bricks are put in any construction with mortar the size becomes 10 inch x 5 inch x 3 inch. The size of walls constructed by bricks in Bangladesh are 3 inch, 5 inch, 10 inch, 15 inch, 20 inch, 25 inch and 30 inch. Hence, mentioned size of bricks can be used safely without any breakage. Therefore, 9.5 inch x 4.5 inch x 2.75 inch brick is considered as standard size and is most economical in engineering constructions in Bangladesh.

7. CLASSIFICATION OF BRICKS

Bricks are classified depending on its quality and durability. There are eight types of bricks. Classification of bricks is shown below:

Ser (a)	Type (b)	Description (c)
1.	First Class Bricks (Grade A)	They should be of uniform size and colour, thoroughly and evenly burnt. They should ring clearly when struck with a hammer or another brick. They should be well shaped with even surfaces and without cracks, rain spots or flaws of any kind. They should not absorb more than one sixth of their wet in water for 24 hours.

Ser	Type	Description
2.	Second Class Bricks (Grade B)	These bricks must possess the hardness and colour of first class bricks but are slightly irregular in shape, size or rough on the surface.
3.	Third Class Bricks (Grade C)	These are bricks which are not sufficiently well burnt sufficiently and of uniform shape and size for use in un in important constructions.
4.	First Class Bats	These are broken bricks of the same quality as first and second-class bricks (Grade A and Grade B).
5.	Second Class Bats	These are broken bricks of the same quality as third class bricks (Grade C)
6.	Picked Jhama Bricks	These bricks are uniformly vitrified throughout, but must be of good shape, heavy and selected quality. They must not be spongy.
7.	Jhama Bricks	These are well-burnt bricks but not quite so well shaped as picked jhama bricks. They must not be spongy and must be free from cinders and projecting flumes of and of fairly good shape.
8.	Jhama Bats	These are broken bricks of the classes picked jhama and jhama bricks

APPENDIX E

STANDARD BRICKS TESTS (BDS-208: 1980)

1. GENERAL

The standard of BDS- 208 (1962) has been accepted by Bangladesh Standards and Testing Institution on 11 July 1980 with prior analysis by clay bricks, cement blocks and hollow blocks department committee and civil engineering department. This standard was first prepared in 1962. While preparation, the views of maker, consumer and technical personnel were given due consideration. This standard was compared with foreign standards for the purpose of export development i.e. IS-1077 (1970), IS-5454 (1969). However, this standard is subjected to modification due to industrial and technological development of the country. Any modification to be done with prior consent and investigation by designated committee. All numerical value of this standard to be published following BDS 103:1960 rules for rounding numerical values. This standard is generally applicable for preparation of different types of bricks for both building bricks and other purposes.

2. SAMPLING PROCEDURE

There are two types of sampling i.e. (a) Random Sampling and (b) Stratified Sampling. Random sampling is carried out in such a manner so that similarity of each item is changed. In stratified sampling procedure a lot is divided into two and random sampling is taken from each lot. Either any of the sampling procedure can be applied, so as to ensure consistency in sampling procedure. In continuous production of bricks, sampling can be done during removal of bricks from stack. In this case each lot to be divided minimum ten or above sections with a view to collects sample from each section. However, if sampling is required to be done from a dumped stack, then samples to be collected from different layers. Numbers of bricks to be taken for sampling depends on the number of bricks in a lot. Number of bricks for sampling and accepted number of faulty bricks per lot is shown below:

Serial	Number of Bricks in a Lot	Number of Bricks in Sampling	Accepted Number of Faulty Bricks
1.	2001-10000	20	1
2.	10001-35000	32	2
3.	35001-50000	50	3

3. TESTING PROCEDURE

3.1 INTRODUCTION

Standard bricks tests include texture, compressive strength, water absorption, weight loss on ignition, firing shrinkage and density of bricks. Sampling procedure as stated to be applied for each category of testing. If test results reflect that number of under quality bricks is same or less than that of qualified bricks then it will be considered to be accepted. On the other hand if number of unqualified bricks are more than qualified bricks then bricks prepared to be considered as unaccepted. Standard size of burnt bricks to be accepted as 24cm x 11.5 cm x 7 cm. However, variation of 1.5mm may be accepted for length up to 5 cm, 3mm for length up to 7.5 cm, 5mm for length up to 10cm and 6mm for length up to 15 cm and above (BDS: 208, 1980).

3.2 CRUSHING STRENGTH TEST

Minimum 12 bricks have to be collected in random from any lot. Each bricks to be divided into half bricks in order to test crushing strength. Each half bricks to be leveled with sulfur lining so that uneven surfaces are made up and pressure is evenly applied on the surface area. Half bricks sample to be placed in between compression plate in such a manner that center of compression plate and center of half bricks coincide. Load of 140 kg/cm^2 is to be applied till such time sample fails. The moment increase of load terminate, it will be considered to be break. Load obtained during break to be divided with minimum cross section area of bricks sample. Standard crushing strength is enumerated below:

Ser	**Grade**	**Average of 12 Half Bricks**		**Average of Individual Half Bricks**	
		Strength (kg/cm^2)	$lb/inch^2$	Strength (kg/cm^2)	$lb/inch^2$
1	A	280	4000	211	3000
2	B	175	2500	140	2000
3	C	105	1500	84	1200

If average strength of 12 bricks is below than that of value as stated above, then bricks of that particular lot to be considered as unsatisfactory. However, if average strength of individual bricks reflects to be lower than that of minimum value, then double number of samples to be collected and 2nd test to be carried out to ascertain accepted result (BDS: 208, 1980).

3.3 WATER ABSORPTION TEST

Minimum six bricks sample to be taken for water absorption test. Bricks sample to be oven dried at 110^0 C for 48 hours (BDS: 208, 1980). After drying these samples will be cooled at normal temperature for two hours. Dry weight of bricks sample to be taken at this normal temperature. Obtaining dry weight, each bricks sample to be submersed under water for 24 hours at 15^0 C water temperature. After water absorption for 24 hours all samples to be taken out from water and wet weight to be taken within 3 minutes.

Water absorption $W = \{(W2-W1)/W1\} \times 100$

Where: W1= Dry weight of bricks

W2 = Wet weight of bricks

According to BDS-208: 1980 accepted water absorption should be within 12% to 16% for A, B and C category bricks.