THE CHARACTERISTICS AND REUSE OF GOLDEN HORN SURFACE SEDIMENT

by

ţ

Zehra Semra Aydın

B.S. in Chem., Marmara University, 1991

Submitted to the Institute of Environmental Sciences in partial

fulfillment of the requirements for the degree of

Master of Sciences

in

Environmental Sciences

Boğaziçi University

1994

Bogazici University Library

ACKNOWLEDGEMENTS

I would like to express my deep gratitude to Prof. Dr. Mehmet Karpuzcu for his great deal of interest, scientific guidance, and encouragement throughout this study.

I am most thankful to Prof. Dr. Ahmet Mete Saatçi for his never ending support and help in the whole work.

I benefitted greatly from the documents of İstanbul Municipality and İSKİ. I am thankful to İstanbul Köprüler Müdürlüğü personnel for their generous assistance during sampling.

Finally, I am most thankful to my husband Kemal Can, for his understanding and unforgettable support throughout the study.

THE CHARACTERISTICS AND REUSE OF GOLDEN HORN SURFACE SEDIMENT

Zehra Semra Aydın

Master of Science in Environmental Sciences, 1994

Advisor: Mehmet Karpuzcu

Keywords: Sediment, dewatering, metal adsorption

In this study the characteristics and reuse of Golden Horn surface sediment were investigated.

40 per cent of the water content of the sediment is free and immobilised water, and the remaining 60 per cent is bound water content. In accordance with these results, the high specific resistance value of the sediment indicates its poor dewaterability characteristics.

The leachate of the samples does not contain the toxic heavy metals even if the deposits get into contact with acid rain of pH 4.

The sediment has strong Cu and Pb adsorption properties. Considering the metal content of the sediment, it is obvious that the sediment is not saturated with these metals.

Another important characteristic of the samples is their high buffering capacity.

The reuse of the dried sediment as a clay mixture in brick manufacturing seems possible.

HALİÇ ÇAMURUNUN KARAKTERİSTİKLERİ VE TEKRAR KULLANILABİLİRLİĞİ

Zehra Semra Aydın

Yüksek Lisans Tezi, Çevre Bilimleri Programı, 1994

Tez Danışmanı: Prof. Dr. Mehmet Karpuzcu

Anahtar Sözcükler: Dip çamuru, kurutma, metal adsorpsiyonu

Bu çalışmada Haliç dip çamurunun yüzeyinden alınan örneklerin karakteristikleri ve tekrar kullanılabilirliği araştırıldı.

Çamurun bünyesinde bulunan nemin yüzde 40'ını serbest (free) ve hareketsiz (immobilised) sular, geri kalan yüzde 60'ını ise bağlı (bound) su oluşturmaktadır. Bu verilerle birlikte özgül direncinin de yüksek olması, çamurun su bırakma özelliğinin zayıf olduğunu göstermektedir.

Alınan numunelerin sızıntı sularında ağır metallere rastlanmamıştır. Çamur pH'sı 4 olan asit yağmuruyla temas etse bile bu durum değişmemektedir.

Öte yandan yapılan çalışmalar sonucu çamurun yüksek Cu ve Pb adsorpsiyon özelliği saptanmıştır. Bünyesindeki Cu ve Pb konsantrasyonları göz önünde tutulduğunda çamurun bu metallere doymadığı görülmüştür.

Numunelerin sahip olduğu diğer önemli bir özellik de yüksek asit tamponlama kapasitesidir.

Kurutulan çamurun tuğla hamuru ile karıştırılarak tuğla imalatında kullanılması mümkündür.

TABLE OF CONTENTS

Page

ACKNOWLEDGEMENTS	iii
ABSTRACT	iv
KISA ÖZET	v
TABLE OF CONTENTS	vi
LIST OF FIGURES	viii
LIST OF TABLES	x
LIST OF SYMBOLS	xi
1. INTRODUCTION	1
1.1. Aims and Objectives	2
2. GENERAL INFORMATION ABOUT GOLDEN HORN ESTUARY	3
2.1. Pollution Sources in the Estuary	3
2.2. The Problem of Bottom Sediments	7
2.3. Information About Sampling	8
3. CHARACTERISTICS OF THE GOLDEN HORN SEDIMENTS	9
3.1. Sediment Dewatering	9
3.1.1. Drying Theory	9
3.1.2. Analysis of Dewatering Characteristics of	
the Golden Horn Sediment	12
3.1.2.1. Specific Resistance to Filtration	12
3.1.2.2. Constant Temperature Drying Method	14
3.1.2.3. Determination of Solid Content of the	
Golden Horn Sediments	18
3.1.3. Sediment Dewatering on a Small Scale Sand	
Bed Model	20
3.1.3.1. Material and Method	23
3.1.4. Metal Analysis of the Dewatered Sediment	27
3.1.4.1. General Information About the Atomic	
Absorption Instrument	29
3.2. Heavy Metal Analysis	30
3.2.1. Digestion of the Samples	
3.3. Trace Metal Uptake Characteristics of the Golden Horn	
Sediment	40
3.3.1. Adsorption Theory	40
3.3.2. Procedure of the Adsorption Experiments	42
3.3.3. Desorption Studies	44

	3.4. Investigation of Reuse Possibilities of the Dried Sediment44
4.	DISCUSSION
5.	CONCLUSION
	REFERENCES

FIGURE 3.14	Comparison of Evaporation from Free Water Surface and Decanted Sediment Surface
FIGURE 3.15	Moisture Content versus Time Curve of Undecanted Sediment
FIGURE 3.16	Moisture Content versus Time Curve of Decanted Sediment
FIGURE 3.17	Total Lead Concentrations
FIGURE 3.18	Total Copper Concentrations
FIGURE 3.19	Total Chromium Concentrations
FIGURE 3.20	Total Nickel Concentrations
FIGURE 3.21	Total Cobalt Concentrations
FIGURE 3.22	Total Zinc Concentrations
FIGURE 3.23	Total Manganese Concentrations
FIGURE 3.24	Total Iron Concentrations
FIGURE 3.25	Copper Adsorption Isotherm of Golden Horn Surface Sediment
FIGURE 3.26	Lead Adsorption Isotherm of Golden Horn Surface Sediment
FIGURE 3.27	Porosity versus Weight Percentage Graph of the Bricks made up of Sediment and Clay Mixture

LIST OF TABLES

TABLE 2.1	Major Previous Industrial Utilities Around the Golden Horn and Their Dominant Pollutant
Ι	Discharges
TABLE 3.1	Moisture Content of The Sediment Samples17
TABLE 3.2	Total and Volatile Solids Content of the Sediment Samples
TABLE 3.3	Working Conditions of the Atomic Absorption Spectrometer
TABLE 3.4	Initial and Final Metal Concentrations in the Dewatered Sediment
TABLE 3.5	Total Metal Contents of the Golden Horn Surface Sediment in mg/L of Wet Sediment40
TABLE 3.6	Results of the Porosity Test of the Bricks

,

Page

LIST OF SYMBOLS

A = Area of filter unit

a,b = Empirical constants of Langmuir Isotherm

c = Solids content of the sediment

 $C_e = Equilibrium$ concentration of the adsorbate

 d_{10} = Sieve size through which 10 per cent of the sand passes

 d_{60} = Sieve size through which 60 per cent of the sand passes

K,n = Experimental constants of Freundlich Equation

 M_{cr} = Critical moisture content

 $M_e = Equilibrium$ moisture content

 M_0 = Initial moisture content

P = Vacuum pressure

R = Specific resistance to filtration of the sediment

 t_{cr} = Time required to reach M_{cr}

U.C. = Uniformity Coefficient

V = Volume of filtrate collected

X = The weight of adsorbed material per unit weight of adsorbent

u = Absolute viscosity of filtrate

1. INTRODUCTION

The water quality of enclosed water areas such as lakes, bays, and inland seas is strongly affected by the sediments on the bottom containing large amounts of pollutants. Their presence is expected to contribute to the existing pollution problem in the area. All efforts leading to the purification of such areas are bound to take into account the impact of the deposited sediments. At present seriously polluted sediments are removed from the water area mainly by dredging operations. The dredged sediments are usually transported to an adjacent reclamation area and allowed to stand in order to reduce the volume of the sediment mainly by gravity settling (Tokunaga, 1990).

The disposal of dredged material must be done in an environmentally acceptable manner. The new physicochemical condition of contaminated dredged material at a disposal site may influence transformations of some pollutants, mainly the trace metals, among readily and potentially available chemical forms. The possible release of sediment-bound toxic metals to bioavailable forms as a consequence of dredging and dredged material disposal has received considerable attention in recent years (Benson, 1991, Gambrell 1980).

The Golden Horn Estuary, due to its available sea and road transportation facilities, became the centre of industrialisation of Istanbul with the onset of the twentieth century. The Municipal services in this part of Istanbul was far behind the demand. So the estuary with very little governmental control has received inputs of wastes from several industries and domestic sources for many years in addition to sediments carried by two streams flowing in. Consequently, erosion and transportation of large amounts of sediments occurred. The sea bottom topography has been adversely affected such that the Golden Horn, once deep enough to permit the largest warships, became a very shallow piece of water where even the most flat-bottomed lighter is forced to follow very delicate and narrow channels. Certain parts of the estuary, such as Silahtar, Kağıthane, have been completely filled (Tezcan, 1977).

Golden Horn is both a natural and a cultural heritage to us. Therefore, we are responsible for leaving it with its original beauty to the new generations.

1.1. Aims and Objectives

Due to the different sources of discharges, the Golden Horn sediments hold several pollutants in its body. They are known to contain high concentrations of trace metals, especially in bottom sediments. They contribute to the pollution in the estuary.

The impact of deposits on pollution of the Golden Horn environment requires attention. The possibility of dredging the Golden Horn sediments has been a topic of recent projects to remedy the deteriorating environmental conditions at the Golden Horn and to facilitate navigation. Before the sediments can be disposed of a large portion of water must be removed. The amount of material to be dredged in Golden Horn is about 2.5 million m^3 . So it is necessary to use the most cost-effective means for dewatering the sediment. One of the more cost-effective means of removing this water is dewatering the sediment by natural means in sand beds. Therefore, the dewaterability characteristics considered in this study are due to dewatering the sediment using any coagulants.

The impact of dredged sediments on the environment and the possibility of reuse of it was the main aim of this research. The objectives of the study were to:

1- Determine the dewatering characteristics of the Golden Horn sediment by natural means,

2- Measure the metal concentrations of the dried sediment and the drainage collected during the dewatering process,

3- Measure the concentrations of important heavy metals (Pb, Cu, Cr, Ni, Co, Zn, Mn, Fe) in the estuary surface sediment,

4- Investigate the trace metal uptake characteristics of the Golden Horn sediment,

5- Investigate the reuse possibilities of the Golden Horn sediment.

2. GENERAL INFORMATION ABOUT THE GOLDEN HORN ESTUARY

Golden Horn is an estuary of two small streams, namely Kağıthane and Alibeyköy, in the European part of İstanbul (Fig. 2.1). It lays 7.5 kilometres inland from the southern end of Bosphorus. Its deepest draft at Galata Bridge location is measured as 42 meters. The widest distance between shores is 900 meters and is measured between Sarayburnu and Tophane. The surface area of Golden Horn is 2,632,000 square meters (Teksöz, 1991).

2.1. Pollution Sources in the Estuary

The history of pollution in the vicinity of Golden Horn goes back to 15th century. The problem was erosion on the hills of Kağıthane and Alibeyköy Creeks and accumulation of eroded material at the bottom of Golden Horn. After 1950, due to the industrial settlements in the vicinity of the estuary, the environmental pollution has started. The rate of pollution increased by the increase in pollution and industrial settlement and the problem developed into an unbearable and unhealthy conditions.

The main causes of pollution may be stated as follows:

1. Industrial Wastes: About hundred plants have been giving their wastes directly to Golden Horn and creeks. The major of these industrial utilities and their dominant polluting discharges are given in Figure 2.2 and Table 2.1. The industrial wastes have been polluting the estuary physically, chemically, and biologically. The pollution due to industrial activities has been calculated to be equal to the pollution due to 3 million population. In 1988, the Istanbul Municipality has started to eliminate the industries around the estuary. Now there are no industries in the immediate vicinity of Golden Horn except for the three dockyards present.



FIGURE 2.1. Locations of the Sampling Stations



FIGURE 2.2 Previous Industrial Utilities Around the Immediate Vicinity of Golden Horn (Karpuzcu, 1975)

TABLE 2.1. Major Previous Industrial Utilities Around the Golden Horn
(Karpuzcu, 1975) and Their Dominant Pollutant Discharges
(Shreve and Brink, 1975)

No	Name	Metal Discharge
1	Boyama Fab.	Cr
2	Yıldız Boyahanesi	Cr
3	Boyateks Tic. ve San.	Cr
4	Altınyıldız Mensucat Fab.	Cr
5	Bahariye Mensucat Fab.	Cr
6	Gislaved Fab.	Cr, Fe, Pb, Zn
7	Türkiye Maden Eşya Fab.	Cr, Cu, Fe, Pb, Ni, Zn
8	Batı Ticaret	Cr, Cu, Fe, Pb, Ni, Zn
9	Trakya San. ve Tic. A.Ş.	Ni
10	İktisadi San. Tes. ve İşlet.	Fe
11	Elektometal San. A.Ş.	Cr, Cu, Fe, Pb, Ni, Zn
12	Kemal Nemli Vida Fab.	Cr, Ni, Fe, Cu
13	Nurmetal San. Tic. A.Ş.	Cr, Cu, Fe, Pb, Ni, Zn
14	İnkilap A.Ş.	Cr
15	Yener İş Mensucat Fab.	Cr
16	Şark Mensucat Fab.	Cr
17	Kulaksızoğlu Tekstil San.	Cr
18	Pil ve Fener San. Ltd. Şti.	Cr, Ni, Cu
19	Birlik Empirme Fab.	Cr
20	Rabak Elektronik Mamulleri	Cu, Pb
	Şakir Zümre Aletleri Koll. Şti.	Cr, Cu, Pb, Fe, Ni, Zn
22	MAS Sanayi Koll. Şti.	Zn, Pb
23	Damas A.Ş.	Fe, Ni, Cr
24	Sabit Boya Fab.	Cr
25	Hasköy Tersanesi	Cr, Ni, Cu, Fe, Zn
26	Hasköy Yün İplik Fab.	Cr
27	Alanya Demir İş Çelik Tel Çivi San.	Cr, Ni, Cu, Fe
28	Elektrik Fab.	Cr

2. Domestic Wastes: The other important pollutant of the estuary is domestic wastes of around 800,000 population in the vicinity. At present the Istanbul Municipality is working on projects to eliminate the discharges to the estuary. The Güney Haliç Interceptor is collecting the discharges to southern part of the estuary, and the Kuzey Haliç Interceptor which will collect the discharges to the northern part is under construction.

3. *Erosion and Sedimentation:* Fine materials of the deep hills of Alibeyköy and Kağıthane Creeks are transported into the estuary, and they sediment at the bottom.

4. Ships and Wrecks: Ships are polluting the estuary by their wastes and abandoned wrecks impede the circulation of water in the estuary (Köseler, 1982, Arıcan, 1977).

2.2. The Problem of Bottom Sediments

There are three main undesired features of the sediment:

- 1. They contribute to the water pollution.
- 2. They impede sea transportation in the area.
- 3. They contribute to the geotechnical problems.

The sediments are almost in a liquid state in the upper 5 to 7 meters zone. Their densities measured in the laboratory have an average value of 1.1 g/cm^3 , and the pH of the wet sediments has a value around 7 - 7.5.

The geographical location of the estuary is providing many facilities in the sea transportation. However the present conditions are not suitable for an efficient sea transportation in the estuary. Therefore, dredging of bottom sediment is necessary to obtain sufficient depth and to prevent pollution of water in the area (Köseler, 1982).

2.3. Information about Sampling

Eleven stations were selected at the Golden Horn, with depths ranging between 20 centimetres at Kağithane to 35 meters at Unkapani location. The locations of the sampling stations are shown in Figure 2.1. The points mentioned below were the logic behind the selection of the sampling locations:

1. The sampling locations were distributed throughout the estuary at equal distances so that the samples represent the whole study area.

2. Representative samples were taken at points where there were important discharge points before the industry was dispatched from the location. (Station numbers 2, 3, 5, 6, 11)

3. Samples were also taken from critical locations such as the existing military dockyard and the bridge floats. (Station numbers 2, 3, 7, 8)

Surface sediment samples were taken on 15^{th} of June , 17^{th} of September 1993 and 15^{th} of January 1994, using an Ekman-Birge type bottom sampler with an effective grasping area of 225 cm². The bottom of the sampler body consists of two spring closed jaws, the mechanism of which is released by a messenger. Two light plates over the opening at the top of the sampler prevent the sample from being washed out while the sampler is being heaved out of the water. The sample containers were polyethylene with polyethylene caps and they were acid rinsed. A portion of each sample was preserved immediately by acidifying with concentrated nitric acid (HNO₃) to pH < 2 for the total heavy metal analysis. Total metals include all metals inorganically and organically bound both dissolved and particulate (APHA, 1989).

The centre of the sampling stations is Unkapani Köprüsü which is the first sampling point. From Unkapani Köprüsü to Hasköy (Station number 5) sampling was realised with a carrier belonged to Köprüler Müdürlüğü. After Hasköy the depth was less than 3 meters. So, sampling was continued with a motorboat until Eyüp (Station number 9), and after Eyüp, sea transportation by any means was impossible as the depth was less than 50 centimetres. Therefore, the samples were taken from the shore.

3. CHARACTERISTICS OF THE GOLDEN HORN SEDIMENTS

The Golden Horn sediments were analysed to determine the recent heavy metal contaminant levels and their dewatering characteristics. Such information is expected to be useful in case the dredged bottom sediments are collected in an accumulation site.

3.1. Sediment Dewatering

The dredged sediments can be transported to an adjacent reclamation area as either a wet slurry or a dry or semi dry solid form. The ultimate disposal is often fascilated by removing enough of liquid portion so that the sediment behaves as a solid rather than liquid. This operation is called dewatering, in other words it is further reduction of the moisture content of the sediment. The advantage of dewatering is that the volume is greatly reduced and handling properties are improved. But it is usually very difficult to remove water from sediments since they strongly hold water. Necessity of a vast reclamation area, formation of soft ground, generation of malodour and noxious insects are unsolved problems in the treatment of polluted sediments (Tokunaga, 1990, Adrian, 1987, Novak, 1975a). It is clearly of some importance to assess the dewatering characteristics of the sediment for the efficiency of the dewatering process.

At present a variety of dewatering methods are in use, such as vacuum filtration, centrifugation, belt filter presses or drying beds. Their applicability are influenced by the type of the sediment. Conventional drying beds are the most widely used means for dewatering, especially in locations where climatic conditions are favourable and enough land is available. In this study a pilot scale drying bed has been used as a model study of dewatering (Tchobanoglous, 1991).

3.1.1. Drying Theory

Dewatering on sand beds can occur in two distinct steps; draining of free water followed by air drying to the point of handleability. Drainage is clearly the more significant factor. It is affected by solids content, dosing depth, depth of supporting media, sand grain size, degree of paving, and the presence or absence of coagulants (Novak, 1975b, Jennett, 1973).

The dredged material undergoes volume reduction through the processes of sedimentation, self-weight consolidation, and evaporative drying in the sand beds. During sedimentation and self-weight consolidation, water is removed upward from the material, and a supernatant is formed on top of the soil material. In the initial phase following material placement, the upward flux of water through the dredged material slurry is at a fairly rapid rate. At this stage a layer of water will remain over the soil material since the formation of water on top of the soil material progresses at a rate faster than the evaporation rate. The supernatant formation rate will slow to a value less than the evaporation rate and eventually the soil surface will become exposed. This represents the beginning of the evaporative drying phase for dredged material.

By gravity drainage, water content is reduced depending on initial solids content. By further reducing the moisture content with evaporation the sediment acts more like a gel and finally as solid. During this later stage the sediment shrinks and cracks. The evaporation can be continued to equilibrium, producing a cake as hard as dry sand.

Dewatering by evaporation occurs in two distinct phases (Fig. 3.1). The initial phase is known as the constant-rate drying period. Evaporation loss at a constant rate continues until the free surface moisture is exhausted and no longer can be replenished by the internal transport of water to the sediment surface. Further evaporation then occurs at a decreasing rate during the period known as the falling- rate drying period. The falling-rate phase may or may not be a linear relationship with time and depends on the nature of the dewatering material. The potential for evaporation from a saturated surface is controlled by the net radiation at the surface, wind velocity, air temperature, and humidity (Benson, 1991, Jennett, 1973, Marklund, 1990).

Typical drying curves for moist solids are given schematically in Figures 3.1. and 3.2. The drying curve illustrated in Figure 3.1 shows the change in moisture content with respect to time, and Figure 3.2 shows the change in drying rate with respect to moisture content.



FIGURE 3.1 A Typical Moisture Content versus Time Curve (Benson, 1991)



Average Moisture Content / Initial Moisture Content



The line between points A and B illustrates the constant-rate drying period, and the line between points B and C shows the falling-rate drying period. Point B is termed the critical moisture content and point C represents the equilibrium moisture content, or that beyond which no further drying occurs (Benson, 1991). The critical moisture content is influenced by the sediment transport rate and the dosing depth. A more intense drying condition requires a higher internal transport rate to maintain a constant moisture loss. For example of two identical samples dried under different conditions, the one dried under a more intense condition will exhibit a higher critical moisture content. Conversely of the two different samples dried under the same conditions, the one having the lower internal transport rate will have a higher critical moisture content (Jennett, 1973).

3.1.2. Analysis of Dewatering Characteristics of The Golden Horn Sediment

The dewatering characteristics of the sediment are essential for the efficiency of the dewatering process. The factors that influence dewatering on sand beds are:

1. Internal sediment characteristics, such as the specific resistance to filtration or sediment solid content;

2. Environmental factors, such as net radiation at the surface, wind velocity, air temperature and humidity.

The internal sediment characteristics are strongly effective on the sediment drainage rate while the environmental factors influence the evaporation from the saturated sediment surface (Novak, 1975).

3.1.2.1. Specific Resistance to Filtration

Specific resistance is a parameter used for measuring the dewaterability of any slurry. It is considered to be the key factor in the characterisation of dewaterability. The laboratory determination of specific resistance involves dewatering a small sample (100 to 300 mL) in a Buchner funnel and applying a constant vacuum of 400 mm Hg. The water released from the sample is collected in a measuring cylinder with the volume accumulated being recorded at known time intervals. The rate of dewatering is a function of the sediment characteristics and the vacuum pressure applied so that

$$dV / dt = PA^2 / \mu (rcV + RA)$$
(1)

where

V : volume of filtrate collected in time t

P : vacuum pressure

A : area of filter unit

 μ : absolute viscosity of filtrate

r : specific resistance to filtration of the sediment

c : solids content of the sediment

R : resistance to filtration of filter unit

At constant pressure, integration of Equation (1) gives

$$t = (\mu rc / 2PA^2) V^2 + (\mu R / PA) V$$
(2)

or

$$t/V = (\mu rc / 2 PA^2) V + \mu R / PA$$
 (3)

Plotting the experimental data in the form of Equation (3) enables calculation of the specific resistance of the sediment from the slope of the line. Figure 3.3 shows the time / filtrate volume versus infiltrate volume curve of the Golden Horn sediment having the equation of

$$t/V = 0.027 V + 0.245 \tag{4}$$

and $R^2 = 0.99$. The calculated average specific resistance value of the sediment sample is 2.5 x 10^{15} m/kg. Specific resistance has units of m/kg and a sample with good dewatering characteristics would have an r value of around 10^{10} m/kg. Poorly dewatering samples have r values of 10^{12} or higher. According to the given range Golden Horn surface sediment is a poorly dewatering sediment (Tosun, 1992, Christensen, 1983, Christensen, 1985).



FIGURE 3.3. Time/Filtrate Volume versus Filtrate Volume Graph of Golden Horn Surface Sediment

3.1.2.2 Constant Temperature Drying Method

Specific resistance to filtration is the main parameter used to characterise the dewaterability of any slurry. It provides an empirical measure of the resistance offered by the solid material to the withdrawal of water. However the amount and type of water present in the sediment sample will also influence its dewaterability. The moisture types in the sediment, in other words the moisture to solid bond strengths, and the relative magnitudes of different moisture types influence the specific energy requirements for solids separation. Knowledge of these is a prerequisite for rational selection of the most cost-effective volume reduction process (Christensen, 1983, Smollen, 1990).

The surface of the sediment particles is covered with a thin film of water. It is called the absorption water, and it is strongly bound to the surface mainly by intermolecular forces. On the other hand in sediments consisting of fine particles, a large amount of water is enclosed within the sediment structure which is called the interstitial water. Interstitial water is not directly bound to particles, existing in a relatively mobile form. Sato et al. (1982) classifies the moisture content as "bound" and "free" fractions. The moisture types can be determined by the constant temperature drying method of Smollen (1987). This method includes drying a small

sample, in this study 3 g of sediment sample was used, under constant temperature (35 °C) and humidity (60 per cent) in a pan with a known diameter. The sample is weighed periodically in every 30 minutes until the sample showed no loss in weight by evaporation, and the mass of moisture evaporated is recorded as a function of time. After the drying rate reaches zero, the sample is transferred to a 103 °C oven for dry solids determination. Smollen defines the mass difference in the sample after drying at 35 °C and 103 °C as the chemically bound water content. The drying rate curve is then calculated. It shows a sharp inflection point which corresponds with the elimination of free water. This point has been defined by Smollen to separate the bound water from free water. The remaining part of the curve showing a decline in evaporation rate is considered to correspond with bound water. There is a good linear correlation between bound water and cake moisture decreasing with decrease in the amount of bound water (Tokunaga, 1990, Robinson, 1992, Smollen, 1987).

A typical constant temperature drying rate curve is given in Figure 3.4.



Moisture Content, M (g/g Dry Solid)



- Mo : Initial moisture content (g water / g dry solids)
- M_{cr}: Critical moisture content (g water / g dry solids) which refers to a sharp inflexion in the drying rate. Since the critical moisture is the average moisture through the sample, its value depends on the rate of

drying, the thickness of the material and the factors influencing moisture movement and resulting gradients within the solid.

- Me : Equilibrium moisture content (g water / g dry solids) which represents the limiting moisture content for given conditions of humidity and temperature and depends greatly on the nature of the solids.
 - tc : Constant-rate period, during which the rate of evaporation remains at its initial level, until a critical moisture content (point C) is reached.

Each Golden Horn sediment sample was dried using the constant temperature drying method defined by Smollen to determine the average critical moisture content, free and immobilised moisture fraction and the bound water fraction of the sediment samples. The average masses of moisture evaporated, average drying rates, and the average moisture contents were calculated. The moisture evaporated versus time graph and the drying rate versus moisture content graphs are given in Figures 3.5 and 3.6 respectively.



FIGURE 3.5. The Graph of Moisture Evaporated versus Time



FIGURE 3.6. Evaporation Rate versus Moisture Content Curve

In Figure 3.6 the x-co-ordinate at point C gives the critical moisture value which is 7.42 g/g Ds. The difference between the x-co-ordinate at point S, which indicates start of the test, and point C is the free and immobilised moisture content of the sediment. Likewise the difference between E, which indicates the equilibrium moisture value, and C is the bound water content. The calculated values of each moisture type are given in Table 3.1., and Figure 3.7 summarises the moisture categories of the sediment.

ABLE 3.1. Moisture Content of the Sedime	TABLE	3.1.	Moisture	Content	of the	Sedime
--	-------	------	----------	---------	--------	--------

Chem. Bound Water	Bound Water Content	Free + Immobilised Water Cont. (g/g Ds)	Total Water Content (g/g Ds)
0.11	7.31	4.69	12.0



FIGURE 3.7 Moisture Categories of the Sediment

Higher free and immobilised moisture fractions correspond with lower specific resistance to filtration measurements. Conversely lower free and immobilised moisture fractions correspond with higher specific resistance measurements (Smollen, 1987). The free and immobilised moisture fraction of the Golden Horn surface sediment is low. Likewise its specific resistance to filtration value is high. On the contrary, the bound water fraction of the sediment is high indicating poor dewaterability and higher cake moisture.

3.1.2.3. Determination of Solid Content of the Golden Horn Sediments

Solid content of any slurry is another parameter which influences its dewaterability. The total and volatile solids tests are the only solids determination normally applied to sediments. Settleable solids determination is also an important design parameter. The procedures outlined in Standard Methods were used for determination of total, volatile and settleable solids determination. The results of the total and volatile solids content determinations of the surface sediment samples are given in Table 3.2, and Figure 3.8 is the plot of this table. The highest total solid content is determined at Kasımpaşa, and the highest volatile solid percentage is measured at Kağıthane.

	Total Solids (g/L)	Tot. Volatile Sol.	Per cent Vol. Solid
(1) Unkapanı	78	12	15
(2) Kasımpaşa	284	45	16
(3) Fener	203	33	16
(4) Hasköy	185	35	19
(5) Hasköy (İskele)	110	19	17
(6) Ayvansaray	211	38	18
(7) Haliç Köprüsü	158	23	14
(8) Haliç Köp.(Kıyı)	76	13	17
(9) Eyüp	231	36	17
(10)Silahtar	206	43	21
(11)Kağıthane	235	59	25

TABLE 3.2. Total and Volatile Solids Content of the Sediment Samples

Percentage of volatile solids are determined by dividing the total volatile solid content into total solid content.

The settleable solid content of the Golden Horn sediments, measured by Imhoff cone, has an average value of 980 mL/L.



FIGURE 3.8. Distribution of the Solid Content within the Surface Sediment

3.1.3. Sediment Dewatering on a Small Scale Sand Bed Model

A model sediment drying bed and an evaporation pan were constructed to measure the drainage and evaporation from the sediment and evaporation from the free water surface having the same surface area. The dimensions were chosen according to the Manual of Practice No.20 of the Water Pollution Control Federation (WPCF, 1969). Figure 3.9 shows the dimensions and construction details of the models. The models are made up of plexy-glass. They are square in plan with dimensions of 23 cm x 23 cm. The drying bed and the evaporation pan are 40 and 20 cm in height respectively. At the bottom of the model drying bed, there is a supporting plate with 2 mm diameter drain holes. The drying bed was filled with sand with an effective size of 2.5 and porosity of 0.35. The depth of sand layer was 4 cm. The initial depth of the sediment in the sand bed was 20 cm. The sand size distribution curve is plotted in Figure 3.10.





/





Supporting Plate at the Bottom

of the Sand Layer

÷





FIGURE 3.10. Sand Size Distribution of the Sand Bed

Uniformity Coefficient, U.C. = $d_{60} / d_{10} = 1500 / 600 = 2.5$

where

 d_{60} : Sieve size in microns through which 60 per cent of the sand passes

 d_{10} : Sieve size in microns through which 10 per cent of the sand passes

3.1.3.1. Material and Method

The drying experiments were run in two stages. In each run the initial depth of sediment layer and the initial weight of the sediment sample placed in the drying beds were 20 cm and 11.5 kg respectively. In the first run all the sediment placed into the sand bed was let to dry at a temperature range of 22-24 °C under laboratory conditions. The weight of the sand bed, the evaporation pan and the drainage were measured daily using a Sartorius QS 16000 B model digital balance of 16 kg loading capacity and 0.5 g sensitivity until crackings in the sediment cake were observed. In the second run, prior to dewatering, the sediment was let to stand for 6 hours in the bed, and the supernatant that formed over the soil material was decanted by siphoning to the point where the settled sediment was. In each run the daily drainage was collected for further analysis of the related metals. Drainage data were directly measured on weight basis. The daily evaporation from the sediment surface was calculated by subtracting the weight of drained water from the daily weight change of the sand bed. The results were plotted as the cumulative volume of drainage versus time (Fig. 3.11), per cent volume of drainage versus time (Fig. 3.12) evaporation from water and sediment surfaces versus time (Fig. 3.13 and 3.14) and moisture content versus time curves (Fig. 3.15 and 3.16) for each run respectively.



FIGURE 3.11 Cumulative Volume of Drainage versus Time Graph of the Sediments in the Drying Beds (Initial weight of the sediment samples was 11.5 kg)



FIGURE 3.12 Per Cent Volume of Drainage versus Time Graph of the Sediment Samples



FIGURE 3.13 Comparison of Evaporation from Free Water Surface and Undecanted Sediment Surface



FIGURE 3.14 Comparison of Evaporation from Free Water Surface and Decanted Sediment Surface



FIGURE 3.15 Moisture Content versus Time Curve of Undecanted Sediment Sample



FIGURE 3.16 Moisture Content versus Time Curve of the Decanted Sediment Sample

As the dewatering characteristics of the sediment indicate, it takes quite long time to dewater the Golden Horn sediment to the point of handleability by natural methods. Decanting the supernatant above the sediment layer decreases the drying period adequately. In the first run, the supernatant was not decanted, and the sediment reached to the point of handleability in one month whereas in the second run it took 15 days until crackings on the sediment surface were observed. At this point the sediment was behaving like a solid.

Referring to Figure 3.11, it is very clear that drainage continues for 10-11 days in the first run whereas it continues for 4-5 days after the supernatant was decantanted. Deviation of sediment evaporation curve from pan evaporation curve in Figure 3.13 shows that the constant rate drying period started on the 17th day and all the supernatant had evaporated. Until the 17th day evaporation from free water surface was the dominant factor causing the moisture losses. In Figure 3.14 deviation from pan evaporation curve starts at the 2nd day.

The last observation of this experiment is that moisture content of the sediment decreases to a smaller value in a shorter period of time when the supernatant is decanted (Fig. 3.15, Fig. 3.16).

3.1.4. Metal Analysis of the Dewatered Sediment

It is essential to know the behaviour of the heavy metals adsorbed by the sediment in the new environment, under new conditions. To gather this information, the concentrations of the toxic heavy metals (in this study, toxic heavy metals refer to Pb, Cu, Cr, Ni, Co, Zn, Mn and Fe) were analysed in the wet sediment placed into the sand bed. After the dewatering process, the same metals were analysed in the sediment cake and in the drainage collected daily. These metals have toxic effects on plant and animal organisms. Their primary sources in wastes and their toxic effects when present in soil and water in excess amounts can be summarised as follows:

Lead (Pb): The primary source of Pb is from the manufacture of Pb-acid storage batteries and gasoline additives. Pb is also used in the manufacture of solders, pigments and paints. The toxicity of Pb is known for many years. Pb toxicity to plants is uncommon but it accumulates in the roots and their consumption by the grazing animals provides the transportation of Pb to the human body. Copper (Cu): Significant amounts of Cu are produced from textile mills and cosmetics manufacturing. High concentrations of Cu in soils adversely affect the plant growth, and its toxic effect in water changes according to the chemical and physical properties of water. The controlling factor in the prevention of Cu in water, plants and animals is the level of Cu in soil.

Chromium (Cr): The sources of chromium in waste streams are from its use as a corrosion inhibitor and from dyeing and tanning industries. Chromium is used in the manufacture of chrome steels and alloys, and in plating operations. Cr is mostly present in the +6 oxidation state, and in this form it is very toxic and mobile in soil. Chromium has been shown to be toxic to plants and animals, and recent studies indicate it may also be toxic to soil micro-organisms. Chromium in human body causes the irritation of the skin, the lungs and the kidneys.

Nickel (Ni): The primary uses of Ni are for the production of stainless steel alloys and electroplating. It is also used in the production of storage batteries, magnets, electrical contacts, spark plugs and machinery. Compounds of Ni are used as pigments in paints. Ni, in trace amounts, has a role in human nutrition. However, there is also a strong possibility that Ni is carcinogenic. Ni in soils have toxic effect to plants.

Cobalt (Co): Co is used in the production of high grade steel, alloys, superalloys and magnetic alloys. It is also used in smaller quantities as a drier in paints, varnishes and inks. Excessive amounts of Co in soil can be toxic to plants. Although Co is required by animals as it is the central atom in vitamin B_{12} , it has toxic effects when introduced to the organism in excess amounts.

Zinc (Zn): Zinc originate primarily from the production of brass and bronze alloys and the production of galvanised metals for pipes and buildings. Other products containing Zn include rubbers, inks and glass. The toxicity of zinc is directly proportional to the pH and the hardness of water. Animals are generally protected from Zn poisoning in the food chain since high concentrations of Zn are phytotoxic. Aquatic animals are more sensitive to zinc.

Manganese (Mn) and Iron (Fe): The major sources of Mn bearing wastes are the iron and steel industries. Other sources of Mn include disinfectants, paint and fertilisers. Manganese dioxide is found in wastes from the production of alkaline batteries, glass, paints and drying industries. The main Fe sources in wastewaters are several metal industries and dockyards. Although the toxicity of Mn and Fe is not significant, it is recommended to remove them from drinking waters from the aesthetic point of view, owing to the oxidation of Fe and Mn to Fe(III) and Mn(IV) states which form colloidal precipitates. Fe also imparts a taste to water which is detectable at very

low concentrations. Excessive amounts of iron sulphate are quite toxic for children (EPA, 1983, Gül, 1989, Sawyer, 1978).

3.1.4.1. General Information About the Atomic Absorption Instrument

Unicam 919 model Atomic Absorption Spectrometer equipped with various multicomponent hallow cathode lamps was used for the metal analysis. To prevent the interference of other metals, each metal was analysed using standard addition technique. The standards of each metal were prepared by dilution from the 1000 ppm stock solutions supplied by the Unicam Company. The working conditions of the Atomic Absorption Spectrometer for each metal are given in Table 3.3. The optimum gas flow rates and burner positions were determined while aspirating standard solutions of the elements.

	Wavelength (nm)	Band Pass (nm)	Detection Limit (mg/L)
Pb	217.0	0.5	0.10
Cu	324.8	0.5	0.041
Cr	357.9	0.5	0.055
Ni	232.0	0.2	0.063
Со	240.7	0.2	0.081
Zn	213.9	0.5	0.013
Mn	279.5	0.5	0.029
Fe	248.3	0.2	0.6

TABLE 3.3. Working Conditions of the Atomic Absorption Spectrometer

The results were interesting, because the concentrations of all the eight metals analysed in the drainage were below the detection limit of the Unicam 919 model Atomic Absorption instrument. The results of the initial and final metal concentrations per 1 g dry sediment basis are given in Table 3.4.

Metals	Conc. In Wet Sediment (mg / g Ds)	Conc. In Dry Sediment Cake (mg / g Ds)
Pb	0.31	0.25
Cu	1.26	1.92
Cr	0.36	0.35
Ni	0.23	0.30
Со	0.14	0.10
Zn	1.04	0.98
Mn	0.59	0.55
Fe	23.0	29.0

 TABLE 3.4. Initial and Final Metal Concentrations in the Dewatered

 Sediment

The discrepancies between the initial and final metal concentrations are due to the sampling error as the sediment is not a homogeneous material.

3.2. Heavy Metal Analysis

Earlier studies have shown that the greater part of the dissolved trace metals introduced to the Golden Horn environment are adsorbed on the particulate material, and they accumulated in the bottom sediments (Orhon, 1978, Erdem, 1988). In case the dredged bottom sediments are deposited in a reclamation area these metals pose a potential toxic risk to plants, animals and humans since they may be released into bioavailable forms as a result of the changes in the physicochemical conditions. The released metals may leak into the surface and ground waters through the effects of rain and snow waters.

At present all the industrial utilities located at both sides of the Golden Horn Estuary are eliminated. There are only three dockyards still working. No industrial and domestic effluents are discharged into the estuary. The majority of the pollution sources due to discharges around the estuary are eliminated, since the Southern Haliç Interceptor collects most of the discharges. However, as there are still industrial discharges into the Kağıthane and Alibeyköy creeks, they continue to carry pollutants into the estuary. To get the recent heavy metal contaminant level of the toxic heavy metals, Pb, Cu, Cr, Ni, Co, Zn, Mn and Fe were analysed in each of the sediment samples (Kocasoy, 1988).

3.2.1 Digestion of the Samples

The samples were digested to reduce interference by organic matter and to convert metal associated with particulates to a form (usually the free metal) that can be determined by atomic absorption spectrometer. As nitric acid will digest most samples adequately ,and nitrate is an acceptable matrix for flame atomic absorption, nitric acid digestion was used (APHA, 1989).

10 mL of the acidified portion of the samples were digested with concentrated nitric acid (65 per cent, Merck) as indicated in the Standard Methods for the Examination of Water and Wastewater. The sample was transferred to a 125-mL conical flask. 5 mL concentrated HNO₃ and a few boiling chips were added to it. It was brought to a slow boil and evaporated on a hot plate to the lowest volume possible before precipitation occurred. Heating was continued, and concentrated nitric acid was added as necessary until digestion was complete as shown by a light-coloured, clear solution. The flask walls were washed down with water, and filtered. The filtrate was transferred to a 100-mL volumetric flask with two 5-mL portions of deionised water, adding these rinsings to the volumetric flask. Then the filtrate was cooled and diluted to 100-mL mark. This solution was used for required metal determinations.

The distribution of each metal analysed within the estuarine surface sediments is given in Figures 3.17 to 3.24. Table 3.5 summarises the total metal contents of the surface sediment of Golden Horn at each sampling point.

The metal concentrations show an increase towards the Alibeyköy and Kağıthane creeks, reaching highest concentrations in sediment samples taken at the outlets of these creeks. This is due to high industrial discharges into these creeks. When the concentrations of this study is compared with the corresponding concentrations of a previous study (Erdem, 1988), the metal levels obtained in this study are significantly lower.



٦

FIGURE 3.17 Total Lead Concentrations



FIGURE 3.18. Total Copper concentrations



.

٩.

FIGURE 3.19 Total Chromium Concentrations



FIGURE 3.20 Total Nickel Concentrations

ŀ



FIGURE 3.21 Total Cobalt Concentrations



FIGURE 3.22 Total Zinc Concentrations

37



FIGURE 3.23 Total Manganese Concentrations



¢

FIGURE 3.24 Total Iron Concentrations

	Pb	Cu	Cr	Ni	Co	Zn	Mn	Fe
Unkapanı	11	6	6	2	15	9	3	166
Kasımpaşa	81	83	42	26	48	127	70	3880
Fener	126	84	43	14	20	111	33	4030
Hasköy	41	127	62	22	15	120	54	3535
Hasköy (İskele)	48	94	27	19	19	94	43	2725
Ayvansaray	49	146	54	33	27	122	79	4185
Haliç Köp.	41	30	9	4	14	29	16	804
Haliç Köp. Kıyı	28	36	7	5	16	33	30	1400
Eyüp	66	111	74	29	52	118	94	3925
Silahtar	65	100	61	27	37	118	81	2485
Kağıthane	99	278	146	65	43	294	145	3815

TABLE 3.5. Total Metal Contents of the Golden Horn Surface Sediment in mg / L• of wet sediment

3.3. Trace Metal Uptake Characteristics of the Golden Horn Sediment

Sediments are the main compartment in the estuarine environment for trace metals and other toxic materials. Trace metals are known to concentrate in sediments of natural aquatic systems, and this accumulation is postulated to be caused by adsorption processes with various geochemical phases such as hydrous metal oxides, clays and organic matter (Davies-Colley, 1984, Oakley, 1981).

3.3.1. Adsorption Theory

Adsorption in general, is the process of collecting soluble substances that are in solution on a suitable interface. The interface can be between the liquid and a gas, a solid, or another liquid. Interface concerned in this study is between liquid and solid. In an adsorption process the interface is called the adsorbent and the material being concentrated is termed the adsorbate.

The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate. Adsorption will continue until such time, the concentration of the solute remaining in solution is in a dynamic equilibrium with that at the surface. The amount of adsorbed material is generally determined as a function of concentration at constant temperature, and the resulting function is called an adsorption isotherm. Mainly an adsorption isotherm is the relationship at constant temperature between the amount of adsorbate per unit weight of adsorbent versus the concentration of the adsorbate in solution. The equilibrium isotherms are usually correlated by Langmuir or Freundlich equations.

Freundlich Isotherm:

The older of these is the Freundlich isotherm, and it is wholly empiric. It has the form of

$$X = K C_e^{1/n}$$
⁽⁴⁾

where

 X : The weight of adsorbed material per unit weight of adsorbent
 C_e : Equilibrium concentration of the adsorbate in solution

K,n : Experimental constants

The constants in the Freundlich equation can be determined by plotting X versus C and making use of Equation (4) rewritten as

 $\log (X) = \log K + 1/n \log (C)$ (5)

Langmuir Isotherm:

The Langmuir isotherm is used to describe single-layer adsorption and can be written as follows again relating the quantities (X) and (C_e)

$$X = (a b C_e) / (1 + b C_e)$$
(6)

where

X : Amount adsorbed per unit weight of adsorbent

a,b : Empirical constants

 C_e : Equilibrium concentration of adsorbate in solution after adsorption

The Langmuir adsorption isotherm was developed assuming that

1. A fixed number of accessible sites are available on the adsorbent surface all of which, all of which have the same energy and that

2. Adsorption is reversible.

Correspondence of experimental data to the Langmuir equation does not mean that the stated assumptions are valid for the particular system being studied because departures from the assumptions can have a cancelling effect.

There are a number of linear forms of the Langmuir equation. One of them is

$$1 / X = (1 / a b C_e) + (1 / a)$$
 (7)

The constants in the Langmuir isotherm can be determined by plotting 1 / X versus $1 / C_e$ and making use of Equation (6) (Tchobanoglous, 1991, Davies-Colley, 1984, Oakley, 1981, Tan, 1987).

3.3.2. Procedure of the Adsorption Experiments

The adsorption of the toxic metals, copper and lead, by the dewatered sediment was studied. Adsorption experiments were run in 250 mL acid-rinsed polyethylene beakers. 10 g of dewatered sediment and 50 mL of stock metal solutions having concentrations ranging between 1-100 g/L, were added into each beaker. The pH was adjusted to 7 by NaOH. Preliminary studies had shown that adsorption kinetics are quite rapid and equilibrium is reached within 1 hour. Therefore, the sediment samples in the beakers were kept in suspension for 2 hours using magnetic stirrers and the resulting equilibrium concentrations were then measured using Atomic Absorption Spectrometer.

The following isotherms were obtained for Cu and Pb respectively at 24 °C (Fig.3.25, 3.26). However, it was not possible to linearize the isotherms by any of the linearization methods, because the Langmuir and Freundlich equations are only suitable if the experiment is based on the same initial adsorbate concentration and adsorbent dosage under which the isotherms were determined (Davies-Colley, 1984).



FIGURE 3.25 Cu Adsorption Isotherm of Golden Horn Surface Sediment



FIGURE 3.26 Pb Adsorption Isotherm of Golden Horn Surface Sediment

These isotherms explain us why Cu and Pb was not detected in the leaches of dewatering process. As can be seen from Figure 3.25 the maximum weight of Cu that 1 g of sediment can adsorb is 0.23 g. However the sediment contains around 2 mg of Cu per 1g of dry sediment. Likewise, from Figure 3.26 the maximum weight of Pb that 1 g of sediment can adsorb is 68 mg which is very much higher than the present concentration which is 0.3 mg per 1 g of dry sediment.

3.3.3. Desorption Studies

The desorption of metals in the sediment under acidic conditions was also studied to see the effect of acidic rain in a reclamation area. Rain water required for this study was collected at Göztepe. The pH of the rain water was 4. By adding HCl to this water, different water samples having pH 1,2 and 3 were obtained. 20 g of dried sediment was received into 4 different 250 mL polyethylene beakers. Into each beaker, 100 mL of rain water with the given pH values were added respectively. The sediments were kept in suspension by magnetic stirrers. During this experiment high buffering capacity of the sediment was observed. In around half an hour after the addition of water, the pH values of each mixture were increasing to 6.5 - 7 which is the original pH of the sediment. HCl acid was added repeatedly until a constant pH reading of the desired value was obtained. After 24 hours the mixtures were analysed for heavy metals. No significant desorption was observed at pH values 3 and 4 as the concentrations were below the detection limit of the Atomic Adsorption Instrument . At pH 1 and 2, the percentages of metals desorbed were 2 and 0.3 respectively.

3.4. Investigation of Reuse Possibilities of the Dried Sediment

The dewatered sediment will create disposal problems. Therefore the feasibility of using dried sediment in ceramics and building and construction related materials manufacturing was investigated.

The investigation of its reuse in ceramics clay, at the Ceramics Department of Mimar Sinan University, showed that the products were easily breaking up, and that the dried sediment is not suitable for using in ceramics manufacturing. The clay used to investigate the utilisation of dried sediment as brick making material was collected from Topsan Tuğla Fabrikası at Sultanbeyli. Ground and crushed dewatered sediments were mixed with the clay in mass ratios of 10, 15, 20, 30, 40 and 50 per cent. A control sample with no sediment was prepared as a reference. Brick samples with dimensions of 40 mm long, 20 mm wide and 10 mm thick were prepared. The samples were then dried in an oven at 100 °C for 24 hours. The dried bricks were fired in a kiln at a temperature of 1,000 °C for about 24 hours. The finished products were tested to determine their porosities (Tay, 1987, Shreve, 1975).

To determine the porosity of brick samples, their dry weight, weight in water and water saturated weights were obtained (Vlack, 1989). Porosities were calculated using the following formula;

Porosity = [(Saturated Wt. - Dry Wt.) / (Saturated Wt. - Wt. in Water)] x 100 (4)

Generally, the lower porous bricks are more durable than those with higher porosity. On the other hand higher porous bricks have lower thermal conductivity. The results of the porosity test is given in Table 3.6 and its graph is shown in Figure 3.27.

Mass Ratio of							
Sediment in Clay	0.0	10.0	15.0	20.0	30.0	40.0	50.0
Per cent Porosity	26	28	32	34	37	42	46

TABLE 3.6. Results of the Porosity Test of the Bricks



FIGURE 3.27 Porosity versus Weight Percentage Graph of the Bricks Made up of Sediment and Clay Mixtures

The maximum percentage of dried sediment that could be mixed with clay for brick making is 40 per cent, because beyond that, bonding of the mixtures is poor. The surface texture of the bricks is uneven beyond 30 per cent mixture. They may not be acceptable for use as facing brick. On the other hand the degree of surface roughness increases with the amount of sediment in the brick. This is due to the organic component of the sediment being burnt off during the firing process.

4. DISCUSSION

The dewaterability characteristics of the sediment showed that the free and immobilised water is about 40 per cent of the total water content and can be easily removed. The bound water is approximately 60 per cent of the total water content and can not be readily removed from the sediment under the disposal conditions expected to be encountered in practice. The specific resistance of the Golden Horn sediment was found to be 2.5×10^{15} m/kg. In literature poor dewaterable slurries have specific resistance values higher than 10^{10} m/kg (Christensen, 1983). Due to its low bound water, high free and immobilised water content and to its high specific resistance value the Golden Horn sediment is low.

The drying period is shortened if the supernatant formed above the sediment layer is decanted after 6 hours settlement. During the dewatering process of the sediment on model sand beds, it was observed that decanting the supernatant formed above the sediment layer after 6 hours, decreased the drying period from 40 days to 27 days (Fig. 3.15-3.16).

The concentrations of toxic heavy metals in the drainage of the drying beds were below the detection limit of the Unicam 919 model Atomic Absorption instrument. This is attributed to the strong heavy metal adsorptive properties of the sediment. The concentrations of metals measured in the wet sediment and in the dried sediment were approximately equal (Table 3.4). These two results obtained, support the fact that the desorption of the related metals does not occur at normal conditions.

When sediment depositions are exposed to acid rain of pH around 4, the drainage does not show any heavy metal concentrations. Thus, the drainage from the sediment deposits are expected to have no metal contamination threat to the environment. However, the deposited sediments will have odour problems due to degradation of its organic content on site.

According to the results obtained from the Cu and Pb adsorption studies, the concentrations of these metals have not reached to their saturation levels in the sediment. The sediment has strongly adsorbed the metals and does not desorp considerably before the pH is lowered to less than 1. This is the indicator of strong metal adsorptivity of the sediment.

The total concentrations of Pb, Cu, Cr, Ni, Co, Zn, Mn and Fe were measured in the Golden Horn sediment samples. The purpose of these measurements were to observe the level of heavy metal concentrations long after the majority of the polluting sources were eliminated. When the concentrations of this study is compared with the corresponding concentrations of a previous study (Erdem, 1988), the metal levels obtained in this study are significantly lower. Thus, it can be concluded that the removal of the pollutant sources have caused a significant decrease in heavy metal levels.

It is also important to notice that, the sediment has a high buffering capacity. As soon as it is in contact with acid rain having pH equal to 4, the pH increases to a value around 6.5 - 7 which is the pH value of the dry sediment.

The reuse of dried sediment in ceramics manufacturing is not possible. Brick manufacturing was investigated by increasing the weight percentage of sediment from 10 to 50 per cent in the clay used to make bricks. The reuse of the sediment in brick manufacturing seems possible. The maximum percentage of dried sediment that could be mixed with clay for brick making is 40 per cent, because beyond that, bonding of the mixtures is poor. The surface texture of the bricks is uneven beyond 30 per cent mixture. They may not be acceptable for use as facing brick. On the other hand the degree of surface roughness increases with the amount of sediment in the brick. This is due to the organic component of the sediment being burnt off during the firing process.

5. CONCLUSION

The conclusion of this study significant for practical application is that when the dredged Golden Horn surface sediment is deposited in a landfill area, about 40 per cent of the free and immobilised water will drain and evaporate easily. However 60 per cent of total water content which corresponds to the bound water content can not be removed readily under the disposal conditions expected to be encountered in practice. All the dewaterability characteristics of the sediment indicate its poor dewaterability.

According to the dewatering studies, the drying period of the sediment is shortened if the supernatant formed above the sediment layer is decanted.

It is important to notice that toxic metals adsorbed by the sediment do not desorp at the disposal conditions even if the sediment deposits are exposed to acid rain, and that the sediment has a high buffering capacity.

The results obtained from the Cu and Pb adsorption studies showed that although the Golden Horn sediment is polluted with respect to these metals, they have not reached their saturation levels in the sediment.

The metal levels obtained in this study are lower significantly lower than corresponding concentrations of previous studies. Thus, it can be concluded that the removal of the majority of the pollutant sources have caused a significant decrease in heavy metal levels in the Golden Horn surface sediment.

The reuse of dried sediment in brick manufacturing seems possible. The maximum percentage of dried sediment that could be mixed with clay for brick making is 40 per cent, because beyond that, bonding of the mixtures is poor.

REFERENCES

1. Adrian, D.D., "The Reliability of Sand Dewatering Beds for Sludge Measured by the Performance Index" International Symposium on Risk & Reliability in Water Resource, 26-28 June 1987, Vol.2, pp. 925-941.

2. APHA-AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 17th ed., Washington, 1989.

3. Arıcan, G., "Haliç'in Taranıp Temizlenmesi", Haliç Sorunları ve Çözüm Yolları Ulusal Sempozyumu Tebliğleri, Boğaziçi Üniversitesi, İstanbul, 11-13 Feb. 1976, pp. 299-302, 1976.

4. Benson, R.E., Sill, B.L., "Evaporative Drying of Dredged Material" Journal of Waterway, Port, Coastal, and Ocean Engineering, ASCE, 117, 216-235, 1991.

5. Christensen, G.L., "Units for Specific Resistance" Journal WPCF, 55, 417-419, 1983.

6. Christensen, G.L., Dick, R.I., "Specific Resistance Measurements: Nonparabolic Data" Journal of Environmental Engineering, ASCE, 111, 243-257, 1985.

7. Davies-Colley, R.J., Nelson, P.O., Williamson, K.J., "Copper and Cadmium Uptake by Estuarine Sedimentary Phases", *Environmental Science & Technology*, **18**, 491-499, 1984.

8. Erdem, E., "The Distribution of Trace Elements In Golden Horn Surface Sediments," M.S. Thesis, Middle East Technical University, 1988.

9. Gambrell, R.P., Khalid, R.A., Patrick, W.H., "Chemical Availability of Mercury, Lead, and Zinc in Mobile Bay Sediment Suspensions as Affected by pH and Oxidation-Reduction Conditions" *Environmental Science & Technology*, 14, 431-436, 1980.

10. Gül R., "Ağır Metallerin Killi Zeminler Tarafından Adsorplanmasının Araştırılması" Ph.D. Dissertation, Fırat Üniversitesi, 1989. 11. Jennett, J.C., Harris, D.J., "Environmental Effects on Sludge Drying Bed Dewatering" Journal WPCF, 45, 449-461, 1973.

12. Karpuzcu, M., "Haliç'te Kirlenme Problemlerinin Etüdü İçin Uygun Bir Matematik Modelin Araştırılması" Ph.D. Dissertation, İstanbul Teknik Üniversitesi, 1975.

13. Kocasoy, G., "Haliç'teki Fabrikaların Kaldırılmasının Haliç'e Kirlilik Açısından Etkileri", 7. Türk-Alman Çevre Sempozyumu Tutanakları, İstanbul, 1988.

14. Köseler, M., "Geotechnical Evaluations of Haliç's Sedimentary Layers" M.S. Thesis, Boğaziçi University, 1982.

15. Marklund, S., "Dewatering of Sludge by Natural Methods" Water Science & Technology, 22, 239-246, 1990.

16a.Novak, T.J., Calkins, D.C., "Sludge Dewatering and Its Physical Properties" Journal of AWWA, 67, 42-45, 1975.

16b.Novak, J.T., Montgomery, G.E., "Chemical Sludge Dewatering on Sand Beds" *Proceedings of American Society of Civil Engineers*, **101**, 1-14, 1975.

17. Oakley, S.M., Nelson, P.O., Williamson, K.J., "Model of Trace-Metal Partitioning in Marine Sediments", *Environmental Science & Technology*, **15**, 474-480, 1981.

18. Orhon, D., Haliç'te Dipsel Çamur Kirliliği ve Uzaklaştırılması Sorunu, İstanbul, Türkiye Bilimsel ve Teknik Araştırma Kurumu, 1978.

19. Robinson, J., Knocke, W.R., "Use of Dilatometric and Drying Techniques for Assessing Sludge Dewatering Characteristics" *Water Environment Research*, **64**, 60-68, 1992.

20. Sawyer C.N., McCarty, P.L., Chemistry for Environmental Engineering, London, McGraw-Hill Company, 1978.

21. Shreve, R.N., Chemical Process Industries, London, McGraw-Hill Book Company, 1975.

22. Smollen, M., "Categories of Moisture Content and Dewatering Characteristics of Biological Sludges" *Proceedings of the 4th World Filtration Congress*, June 1986, Vol. 2, pp. 35-41, 1987.

23. Smollen, M., "Evaluation of Municipal Sludge Drying and Dewatering with respect to Sludge Volume Reduction" *Water Science & Technology*, **22**, 153-161,1990.

24. Tan, T.C., Teo, W.K., "Combined Effect of Carbon Dosage and Initial Adsorbate Concentration on the Adsorption Isotherm of Heavy Metals on Activated Carbon", *Water Research*, 21, 1183-1188, 1987.

25. Tay, J.H., "Bricks Manufactured From Sludge", Journal of Environmental Engineering, ASCE, 113, 278-283, 1987.

26. Tchobanoglous, G., Burton, F.L., Wastewater Engineering Treatment, Disposal and Reuse, New York, Metcalf & Eddy Inc., 1991.

27. Teksöz, G., Yetiş, Ü., Tuncel, G., Balkaş, T.I., "Pollution Chronology of the Golden Horn Sediments" *Marine Pollution Bulletin*, **22**, 447-452, 1991.

28. Tezcan, S., Durgunoğlu, T., Tuğcu, N., Environmental Study of the Golden Horn A Master Plan, Boğaziçi Üniversitesi, 1977.

29. Tokunaga, S., "Analysis of Dewatering Characteristics of Lake and River Sediments" *Water Science and Technology*, **23**, 1969-1978, 1990.

30. Tosun, İ., Yetiş, Ü., Willis, M.S., Chase, G.G., "Specific Cake Resistance: Myth or Reality", *Wastewater Sludge Dewatering Conference*, June 29-July 1, pp. 1-11, 1992.

31. U.S. Environmental Protection Agency, "Hazardous Waste Land Treatment" Solid and Hazardous Waste Research Division, Municipal Environmental Laboratory Office of Research and Development, April, 1983.

32. Vlack, L.H., Elements of Material Science and Engineering, London, Addison-Wesley Publishing Company, 1989.

33. Water Pollution Control Federation, "Sludge Dewatering" Manual of Practice No. 20, Washington, 1969.