Accelerated carbonation of contaminated sediments and its application

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ACCELERATED CARBONATION OF CONTAMINATED SEDIMENT AND ITS APPLICATION

BY

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THESIS

Submitted to the University of New Hampshire in Partial Fulfillment of the Requirements for the Degree of

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ABSTRACT

ACCELERATED CARBONATION OF CONTAMINATED SEDIMENTS AND ITS BENEFICIAL USE APPLICATION

by

Ketaki Tarabadkar

University of New Hampshire, December, 2009

In United States, every year approximately 300 million cubic yards of sediments are dredged in order to improve the shipping navigation and deepen the harbors. Out of these dredged sediments, approximately 3 - 12 million cubic yards sediments are contaminated. Disposal of clean sediments has various possibilities but contaminated sediments require special and expensive treatments.

The current research aims at utilization of mildly contaminated sediments in positive way in order to find better management techniques. Ideally, solidification and stabilization of the sediments would allow them to be used in beneficial use application. Artificial aggregates were prepared using accelerated carbonation technique in which mixture of sediments, water and portland cement was carbonated in 100% carbon dioxide atmosphere. Accelerated carbonation
technique facilitated sequestration of carbon dioxide, thereby enhancing the properties of the material. Statistical technique was applied to analyze various artificial aggregate mixtures. In order to determine the key process parameters for process optimization, small scale experiments were performed. The optimum mixture obtained was 55% sediments, 25% portland cement and 20% water. The mixture was carbonated for 2 hours in tumbler to produce artificial aggregates. Full scale experiments were carried out on optimum mixture taking into consideration key process parameters. For the suitability of these artificial aggregates in highway environment different kinds of analyses were performed to ensure solidification and stabilization of contaminated sediments. The characterization of artificial aggregates included particle size analysis, modified Proctor test, California Bearing Ratio test scanning electron microscopy, Thermogravimetric analysis and pH dependent leaching test. Particle size analysis revealed that artificial aggregates were uniformly graded. The CBR value of 40.4 was obtained which was within the range of GW type material. Scanning electron microscopy along with Thermogravimetric analysis suggested that higher percentage of clay in the sediments caused formation of two distinct layers in an aggregate obstructing the uniform formation of CaCO₃. The pH dependent leaching test results showed reduction in the release of metals in carbonated artificial aggregates that uncarbonated raw sediments. Finally, it was concluded that artificial carbonation of contaminated sediments can create artificial aggregates and they can be used in beneficial use application.
CHAPTER 1
INTRODUCTION

Sediments are composed of soil, sand, minerals and organic matter washed from land that have settled at the bottom of the water bodies. Sediments are the result of erosion and decomposition of organic material. The accumulation of sediments in the navigational channels can impede shipping and pose a threat to safe navigation. Periodic dredging of sediments is important in order to improve shipping navigation and to deepen harbors. Approximately 300 million cubic yards of sediments are dredged annually in the United States and of these 300 million cubic yards; approximately 3 – 12 million cubic yards are sufficiently contaminated which require special handling and disposal. While there are a number of possibilities for using the clean sediments in beneficial use applications; the contaminated sediments require special and often expensive disposal techniques. This research looks at the use of a new solidification/stabilization technology that would allow mildly contaminated sediments to be used as construction material.

1.1 Current Sediment Management Options

Sediments are habitat for aquatic life, including worms, mussels, clams
and insects. At the same time, chemical contaminants are often found trapped in these sediments because of the presence of organic carbon and minerals. The U.S. EPA has defined contaminated sediments as "soils, sand and organic matter or minerals that accumulate on the bottom of water body and contain toxic and hazardous material that may adversely affect human health or the environment" (USEPA 1998).

Contaminated sediments may be brought to land through maintenance dredging, or through environmental dredging. Environmental dredging is the process in which contaminated sediments are removed from a site specifically to clean the area of contamination. Environmental dredging is followed by treatment and disposal. Ex-situ management methods for contaminated sediments have traditionally included open water disposal, confined disposal facilities and beneficial use of dredged sediments (USEPA/USACE 1992).

In this research we are specifically dealing with dredged sediments. In 1972, the Marine Protection, Research and Sanctuaries Act (MPRSA, also known as the Ocean Dumping Act) was declared to prohibit the dumping of any type of material (including sediments) that would adversely affect human health, ecological systems and marine environment. Essentially, clean dredged sediments are dumped in the ocean with a permit issued by U.S Army Corps of Engineers, using the EPA's environmental criteria. Criteria for ocean dumping of sediments imposed by U.S. Army Corps of Engineers and EPA are very strict. Most of the mildly contaminated sediments from maintenance or environmental dredging are not suitable for ocean dumping.
For contaminated sediments, confined disposal is one of the most commonly used management alternatives. Confined disposal facilities (CDFs) are dike like structures in which contaminated dredged sediments are placed. Although CDFs are commonly used for the disposal of highly contaminated sediments, the high cost involved in design, construction and operation of CDFs and the cost involved in treatment of contaminated sediments prior to placement makes CDFs less suitable for mildly contaminated sediments. The size, design and level of complexity of these confined disposal facilities depend on dredging quantity, sediment contamination level, leaching potential, state and local laws and regulations. In addition, population growth near the coasts means that new CDF sites must often be some distance from the site, so transportation of the sediments to CDF is becoming costly.

The beneficial use of clean dredged sediments is one of the attractive management techniques as dredged sediments are considered a resource instead of a waste. The clean sediments are beneficially used in nourishment of beach, construction fill, landscaping, wetlands enhancement etc. However, decontamination and the beneficial use of mildly contaminated sediments are not very common and are still in the research phase.

There are different factors which should be considered before adopting an appropriate remediation technology for management of sediments. The dredged sediment management options depend on different factors like

- level and nature of contaminants,
- selection of dredging site and potential placement site,
• costs and risks associated with dredging, transportation and disposal,
• environmental acceptability,
• legal constraints.

The treatment of dredged sediments refers to physical, chemical or biological processes used to improve the physical properties and to immobilize the contaminants within the sediments. Ideally, solidification and stabilization of the contaminated sediments would allow them to be used in beneficial use application.

1.2 Project Objective

The objective of this project is to develop an innovative management technique for the beneficial use of mildly contaminated sediments as an environmentally-benign construction material. The focus is given to mildly contaminated sediments that do not require complex and expensive treatments like highly contaminated sediments, but are too contaminated to be used for projects such as wetlands reclamation. This project is divided into three phases. First is the application and refinement of a new solidification/stabilization technology; second is the physical characterization of the treated sediments to determine how they can be used as a construction material (e.g. as an aggregate in the highway environment or as a soil-like fill). Roadways have a high potential for large volume usage of recycled material. Finally, the last phase evaluates the potential environmental impact of the treated contaminated sediments (i.e. leaching potential).
Stabilization/solidification (S/S) technology is one of the most common treatment alternatives due to its simplicity (Jones et al. 1997). Stabilization refers to limiting the mobility of contaminants by transforming them into more stable form and solidification is the improvement of the physical properties of the material (Weimer 2003). S/S involves mixing a binding agent into soil or waste to create a solidified and stabilized product. However, careful designing of soil-stabilizer mixes is important as there could be a risk of negative environmental impact due to degradation in long term (Liu et al 2006). Traditionally, S/S treatment was done using lime, cement, sometimes mixed with fly ash or cement kiln dust as a binder. These binders were used mainly because of their nonproprietary nature and ease in availability. Addition of portland cement results in formation of high strength material. Lime/fly ash used in combination produce low-strength cementation and kiln dust addition eliminate free liquids and usually form a low-strength solid (Fleming et al. 1991).

In the S/S treatment with cement, the mechanism involves the hydration reaction of the cement, the resulted hydrates and the interaction between hydrates and waste material particles (Chew et al. 2004). The major hydration products are calcium-silicate-hydrate (C-H-S), hydrated lime (calcium hydroxide) and calcium aluminate hydrate (C-A-H). The amount of hydrates can be estimated from the chemical analysis of the hydration reactions however, complete hydration is in general impossible (Zhu et al. 2007). While in the process of traditional S/S treatment, initial strength development was controlled by the cement hydration, carbonation reaction was favored at later stage with the
decrease in the cement content and increase in the porosity of the blended material (Cizer et al. 2006). Intentional carbonation may also improve strength and hardness and reduce permeability of the material. In this process, carbonation of the material is the primary reaction and if the supply of CO\textsubscript{2} is stopped hydration of the binder is secondary reaction. Carbonation involves conversion of oxides and calcium hydroxide (Ca(OH)\textsubscript{2}) to calcium carbonate (CaCO\textsubscript{3}). It is being used to treat contaminated soils, municipal solid waste incineration (MSWI) residue etc. in the process of stabilization/solidification. In the process of carbonation, carbon dioxide in the ambient air penetrates the material and reacts with the hydroxides (such as calcium hydroxide) or oxides (such as calcium oxide, magnesium oxide) to form carbonates. Carbonation of the material helps to form a soil/CaCO\textsubscript{3} matrix, enhancing the physical properties and reducing leaching potential. Natural carbonation is a slow process, so much of the initial work focus on utilizing accelerated carbonation techniques. Accelerated carbonation is the intentional application of carbon dioxide during processing of the mixture to increase the rate and extent of carbonation. Accelerated carbonation is being used successfully in UK to treat contaminated soils (Bernard et al. 2005). The difference in accelerated carbonation and traditional S/S treatment method is discussed in Chapter 2. The objective of this research is to use accelerated carbonation as a S/S technology for the treatment of mildly contaminated sediments. The main advantage of this technique over traditional S/S treatment, in which long curing time may be required as opposed to carbonation in which treated waste material is available for development
immediately (Bertos et al. 2004). A number of chemical and physical differences influence the efficiency of treatment technology between soils and sediments. The distinguishing characteristics of sediments from soils are moisture content, particle size distribution, organic content, contamination concentration, mix of contaminants, salt content and material handling (Timberlake 1997). For example, moisture content in sediments is higher than that of soils; sediments often contain a high percentage of fines (silts and clays) which poses difficulties in treatment process. All the above mentioned factors makes the contaminated sediment treatment challenging. This research deals with production of artificial aggregates by mixing contaminated sediments with some kind of cementitious material (binder) and carbonating the mixture. The goal of using accelerated carbonation is to lower the leaching potential of the sediment while creating artificial aggregate for the beneficial use application.

To assess the potential use of contaminated sediments in the form of artificial aggregates, a mixture design experiment approach was developed. With the help of the statistical software package JMP®, optimum experimental points were selected in the mixture space. Optimization of the process as well as optimization of mixture was attained by testing the carbon dioxide uptake capacity of each mixture. The optimum mixture was tested for physical properties and chemical properties to ensure the environmental impact of treated contaminated sediments.
1.3 Significance of the Project

As discussed earlier, management of mildly contaminated sediments is a very challenging task. This research aims at stabilization/solidification of mildly contaminated sediments to form artificial aggregates using accelerated carbonation technology. The focus of the work presented in this thesis is on the creation artificial aggregates and the evaluation of the physical properties and environmental properties of the artificial aggregates to ensure the suitability of these aggregates as a construction material.

In this research, binding agents containing calcium silicate hydrate, calcium oxides (CaO) like coal fly ash (class F) (CFA-F), cement kiln dust (CKD) were used as a binder in preliminary studies. Use of these materials promotes use of recycled materials. The process of accelerated carbonation consumes carbon dioxide by sequestration, thus potentially contributing in the reduction of green house gas emissions.

Using the sediment in the form of artificial aggregates can resolve some of the environmental related issues, like management of dredged sediment, reduction of CO₂ by sequestration, improvement in heavy metal retention in contaminated sediments and to some extent reducing the demand for natural aggregates.

This thesis is divided into five chapters. Chapter 2 presents relevant background information on dredged sediments, portland cement solidification/stabilization techniques and accelerated carbonation techniques. Chapter 3 provides a description of materials selected for this research as well as
the methods used for the treatment, production and analysis. Also, the statistical methods used to design experiments are discussed in Chapter 3. Results from optimization processes and analysis of material for physical and environmental properties can be found in Chapter 5. Finally, Chapter 6 covers the conclusions reached during this research, and provides suggestions and possible future work in this research area.
CHAPTER 2

LITERATURE REVIEW

This chapter discusses the relevant literature related to dredged sediment management in terms of beneficial use applications. The treatment method adopted in this research, called "accelerated carbonation technique" is discussed in detail in Section 2.3. Based on the previous work presented in the literature, the method of solidification/stabilization using accelerated carbonation is compared to conventional solidification/stabilization is also covered in this chapter.

2.1 Dredged Material

Several hundred million cubic yards of sediments are dredged every year from United States ports, harbors and channels to maintain and improve navigation for different purposes, such as national defense, commercial use and recreation. Traditionally, disposal of the dredged sediments consisted of confined disposal facilities (CDFs) and open water disposal. The US Army Corps of Engineers (USACE) have reported, "The results of water quality monitoring have confirmed that CDFs are highly efficient in retaining the sediment solids and attached contaminants" (Miller 1998). However there are some issues which
discourage the use of CDFs. Many of the CDFs are nearing or exceeding design
capacity. There is an increased demand for CDFs to manage contaminated
dredged sediments. Acquiring land for CDFs is a major issue as the land
available near dredging projects is either too valuable or not suitable for CDFs or
is already in use. More stringent environmental regulations posed by government
have increased the costs of new CDFs.

The other traditional disposal method, open water disposal, also has some
issues regarding environmental safety. In 1972, the Marine Protection, Research
and Sanctuaries Act (MPRSA) was passed, which prohibited the ocean dumping
of any material that would unreasonably degrade or endanger human health
and/or the marine environment. Ocean dumping of dredged material is only
allowed under a permit issued by USACE. The closure of traditional ocean
dumping sites, limitations by the clean water act (CWA) and MPRSA on new
dumping sites, and a shortage of suitable upland disposal sites have caused a
crisis for contaminated sediment management programs (Jones et al. 1998).

During the 1970's and 1980's the Corps of Engineers actively started
using clean dredged material for beneficial uses that included environmental
improvements and reclamation projects like habitat development, beach
nourishment, shoreline stabilization and corrosion control, construction and
industrial use etc. (USACE 2003, Krause and McDonnell 2000). In United States
and in some of the European countries dredged material is used as construction
material depending on the type of sediments. For example, in France, it has been
shown that dredged sediments can be reused in sub-base for road construction
Sand and gravel size sediments can be used as concrete aggregates, sand size sediments can be used in bituminous mixtures and mortars, clays with less than 30% sand can be used in the production of bricks, pellets of clays are used as lightweight backfill or aggregates (USACE 2004). Because of growing demand of construction material this may prove to be important beneficial use.

Whether the dredged sediments are highly contaminated, mildly contaminated or clean, it is important to treat them for high physical characteristics and/or for having better control over leaching behavior. Consequently, the use of stabilization/solidification treatment method is needed.

With the growing knowledge of the engineering/environmental properties of the dredged sediments, clean sediments are being used beneficially in more and more projects. However, beneficial use options that incorporate mildly contaminated sediments are still in the development phase, while beneficial use of clean sediments is standard practice (Peterson and Bishop, 2005). The contaminants, combined with the physical properties of sediments, make the beneficial reuse a challenging task.

2.1.1 Engineering Properties of Dredged Sediments

Typically, sediment properties show significant differences in the physical, engineering and environmental properties of dredged sediments depending on the geographical location of the dredging site (Justus 2001). Properties like grain size distribution, specific gravity, water content (natural and dredged), Atterberg limits, organic matter content and level of contaminants make the disposal and/or
treatment of dredged sediments challenging. In general, sediments can be
characterized as: rock, gravel and sand, hard clay, silt/soft clay and mixture
(rock/sand/silt/soft clay) (USACE 2004). Depending on the type and
characteristics of the dredged material, it is used in different beneficial
applications for example agricultural/product application, engineering application,
environmental enhancement etc. (USACE 2004).

The grain size of dredged sediments is one of the most important
characteristics to be determined as the beneficial use and the treatment method
depends on it. Contaminants tend to bind to the smaller/finer fraction of
sediments; hence this fraction is likely to have a higher percentage of
contaminants. In general sediments predominantly consist of sands and silts with
5-10 % clay and 5-7 % organics (USACE 1995a). Table 2.1-1 shows the
beneficial use of sediments with respect to grain size distribution. Typical bay
sediments are mixture of rock, gravel and sand, clay and silt. This research is
more focused on utilization of mixture type sediments hence; we are not
considering the first four types of sediments given in the Table 2.1-1. As shown in
the Table 2.1-1, mixture can be used for almost all types of beneficial uses
except for shore protection and beach nourishment. Soft shore protection has
typically entailed the use of materials such as gravel, sand, logs, and root
masses to absorb wave energy (Johannessen 2000a). Sediments with high
percentage of silts or soft clays are not suitable for shore protection. Also, gravel
and sand are the best suited for beach nourishment; and not the sediments
containing significant fines.
Table 2.1-1: Beneficial use option by material type (USACE 2004)

<table>
<thead>
<tr>
<th>Beneficial Use Options</th>
<th>Dredged Material Sediment Type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rock</td>
</tr>
<tr>
<td>Agricultural/Product Uses</td>
<td></td>
</tr>
<tr>
<td>Construction Materials</td>
<td>•</td>
</tr>
<tr>
<td>Aquaculture</td>
<td></td>
</tr>
<tr>
<td>Topsoil</td>
<td></td>
</tr>
<tr>
<td>Engineered Uses</td>
<td></td>
</tr>
<tr>
<td>Land Creation</td>
<td>•</td>
</tr>
<tr>
<td>Land Improvement</td>
<td>•</td>
</tr>
<tr>
<td>Berm Creation</td>
<td>•</td>
</tr>
<tr>
<td>Shore Protection</td>
<td>•</td>
</tr>
<tr>
<td>Replacement Fill</td>
<td>•</td>
</tr>
<tr>
<td>Beach Nourishment</td>
<td></td>
</tr>
<tr>
<td>Capping</td>
<td></td>
</tr>
<tr>
<td>Environmental Enhancements</td>
<td></td>
</tr>
<tr>
<td>Wildlife Habitats</td>
<td>•</td>
</tr>
<tr>
<td>Fisheries Improvements</td>
<td>•</td>
</tr>
<tr>
<td>Wetland Restoration</td>
<td></td>
</tr>
</tbody>
</table>

US EPA has established four national goals to manage the problem of contaminated sediments, first prevent the amount of contaminated sediments from increasing, second reduce existing volume of contaminated sediments, third ensure dredged sediments are managed in an environmentally sound manner and finally develop scientifically sound sediment management tools (USEPA 1997). Many Superfund and other hazardous chemical sites contain
contaminated sediments that are hazardous to public health and/or the environment. Based on US EPA testing procedure, if the sediments are deemed to be a “hazardous waste”, they must be disposed into US EPA Subtitle C hazardous waste landfill (Lee et al. 2005). Subtitle C landfill is that accepts hazardous waste (USEPA 2008). However, frequently Superfund and other hazardous chemical sites contain sediments that are not classified as “hazardous wastes”, but are, nonetheless, hazardous to public health and or the environment (Lee et al. 2005). Hence, these sediments cannot be considered as clean sediments. Usually, US EPA include the remediation plans for such so-called “non-hazardous” contaminated sediments by landfilling these sediments at a minimum-design Subtitle D landfill which accepts non-hazardous waste (Lee et al. 2005). These sediments fall into category of mildly contaminated sediments. Landfilling of mildly contaminated sediments is expensive and can pose threat of groundwater contamination. Regulations posed by USEPA and USACE restrict the beneficial use of contaminated sediments where it might endanger human health and/or marine environment whilst clean sediments can be utilized easily. Sediments with high organic and inorganic contaminants, which are labeled as “hazardous wastes” are disposed in CDFs or Subtitle C landfills and clean sediments which do no cause impact on public health and environmental quality, are used in beneficial use applications. This leaves the range of so called “non-hazardous” i.e. mildly contaminated sediments that must be considered in terms of risk and reuse. This narrows the area of research to beneficial use of mildly contaminated sediments as a construction material. Details are discussed in
Section 2.2. Mildly contaminated sediments used as a construction material in
the subbase of roads has two major benefits, 1) There is no direct contact and 2)
Encapsulation of contaminants pose no danger to environment.

Typically, the specific gravity of dredged sediments range from 2.6 to 2.8
and is assumed to be 2.65 when not known (Dermatas et al. 2003). Specific
gravity values of dredged sediments are required to determine void ratio,
hydrometer analyses and for consolidation testing (USACE 1987).

The natural water content of sediments is often very high and the water
content of dredged sediments is significantly higher than in-situ water content.
This is due to introduction of additional water in the sediments while dredging
operations. The water content of the sediments ($W_c = W_w/W_s \times 100\%$) can range
from approximately 85 to 900% depending on the dredging technique used
(USACE 1983, Dermatas et al. 2003). For the improvement of the physical
properties of the sediments it is important to have better control over the water
content. Also, if sediments are contaminated, the leachate from sediments must
be collected and treated. (Yamasaki et al. 1995) High water content is very
challenging characteristic of dredged sediments as it is time consuming and very
expensive to remove water from dredged sediments.

It is important to evaluate the Atterberg limits of sediments in order to
determine the plasticity of the dredged sediments. Atterberg limits are
determined in terms of Plastic limit (PL), Liquid limit (LL) and Plasticity index (PI =
PL-LL). The natural water content of the sediments is very high. Liquid limit,
plastic limit and resulting plasticity index characteristically are 65%, 35% and
30%, respectively. Typically, sediments are like viscous fluid with no or little strength (Dermatas et al. 2003). The liquid limit as the plasticity index is directly proportional to organic content of the sediments. The effect of decreasing the organic content on the Atterberg limits is more significant and both the liquid limits and the plastic limits decrease (Zentar et al. 2008). Also, the large amount of fine fraction is consistent with the high plasticity index (Dermatas et al. 2003).

The high organic content makes the stabilization/solidification treatment with cement very challenging. The presence of organic matters can constitute a problem in the process of cement hydration (Kujala et al. 1996). It is observed that different types of organic matter can interact with cement and can decrease the strength (Clare and Sherwood 1954). During the hydration phase of cementitious material, organomineral complex which is often found in organic soils or sediments, breaks up with increasing pH, releasing organic matter. This restricts the calcium ions to participate in the formation of hydrates (Dubois et al. 2008). Hence, it is very important to determine the organic content of the sediments. The quantity of organic matter contained in the sediments can be measured by loss on ignition method according to ASTM. Specific studies on the effects of organic matter content on the consistency limits of dredged sediments has shown significant effect on plasticity index (Zentar et al. 2008).

In addition to physical properties it is important to determine the environmental properties of the dredged sediments.
2.1.2 Environmental Properties - Leaching

Fine grained dredged sediments are often contaminated with heavy metals and organic compounds. The remediation technologies necessary to treat dredged sediments are typically based on soil remediation techniques such as particle size separation, thermal treatments, bioremediation, stabilization/solidification etc. (Dalton et al. 2004; Seidel et al. 2004; Vanthuyne et al. 2003; Weinstein and Weishar 2002; Hisenveld 1991). Dredged sediments are mostly fine grained which cause the heavy metals to strongly bound to fine particles of sediments hence applying soil remediation techniques directly to dredged sediments can be difficult (Mulligan et al. 2001). Several leaching tests have been used to characterize the leaching behavior of the contaminated sediments. Leaching of contaminants are influenced by several factors like pH, redox potential, liquid-to-solid ratio (L/S), contact time and element chemistry (van der Sloot et al. 1996). The pH dependent leaching is one of the efficient methods used to determine the leaching behavior of the sediments at various environmental conditions such as acidic environments, natural soil, soil liming and cement stabilization (van der Sloot et al. 2000). Leaching potential of dredged sediments has been evaluated at different pH values for environmental assessment of reuse and disposal scenarios (Karius and Hamer 2001).

2.2 Stabilization/Solidification Treatment of Sediments

Solidification/stabilization (S/S) technology has been in practice for years to treat contaminated, hazardous material. Solidification/stabilization was used to
treat nuclear wastes in the 1950's, and from the 1970's onward this treatment was to treat wide range of hazardous wastes (Conner 1990).

Solidification/stabilization of contaminated material involves mixing the material with one or more binding/stabilizing agents to produce a more environmentally acceptable product. It is well known that binders interact with various materials, whether chemical compounds in the waste or waste material itself. Compatibility between binder and waste material is the most important aspect in the selection of appropriate binders in S/S treatment (Al-Tabbaa and Perera 2003). Solidification/stabilization treatment includes wide range treatment methods in which chemically as well as physically stable matrices are formed. S/S treatment methods were originally used for treatment of soils.

Solidification refers to an improvement in physical properties to make stable mass (Weimer 2003). Solidification not necessarily involves a chemical reaction between contaminants and stabilizing agent. The product of solidification may be a massive block, clay like material or granular material (EPA/542-B-99-002). Solidification results in smaller volume/surface area which will reduce the volume occupied at disposal site. Reduced volume will reduce the rate of release of contaminants. Solidified material generally will not contain free liquid, which simplifies the handling and transportation of the material. The extent of solidification can be characterized by measuring the unconfined compressive strength tests of the treated material (Batchelor 2006).

Stabilization refers to chemical binding of contaminants to restrict the mobility of contaminants. Stabilization does not necessarily involve any physical
changes in the material (USEPA/542-B-99-002). Stabilization takes place when the contaminants changes from dissolved (mobile) to solid (immobile) phase by reactions such as sorption, precipitation or substitution. All these reactions are affected by pH (Batchelor 2006).

The combined process of solidification/stabilization (S/S) immobilizes the hazardous constituents both physically and chemically with the help of binder.

2.2.1 Stabilization/solidification with Cement

The most commonly used stabilizing agents/binders are cement, lime, various kiln dusts, blast furnace slag (BFS) and pulverized fuel ash (PFA). Most of these binders are alkaline. Portland cement, which binds contaminants and increases strength is the most common binder used to treat contaminated material (Tommaseo et al. 2000). The cement composition, mainly the amount of calcium silicate hydrate (CSH), is responsible for strength development (Hills et al. 1996). It is difficult to make distinctions between purely chemical and purely physical mechanism as both are interrelated processes that occur simultaneously (Glasser 1997). Portland cement can be combined together with lime, BFS, fly ashes etc. to treat the contaminated material. The chemical property of hydration of portland cement is used to lower the solubility of toxic contaminants in the waste. A major factor in applying cement-based S/S technique for the treatment of waste is to extent to which components of waste interact with cement hydration reactions. Many of the compounds like organics, halides, metals and sulfate can accelerate or retard the cement hydration process (Taylor 1990; Conner 1990; Lea 1971, Means et al. 1995; Hills and Pollard 1997). There are
many advantages of using the portland cement as binder. The performance of portland cement is proven and well documented in U.S. since 1950's. It has been used to treat a wide range of wastes, more than any other stabilizing agent/binder. It is commonly available in all parts of U.S. and it is economical. As portland cement is manufactured to exact specifications, it ensures the uniformity (PCA 2004).

2.2.2 Hydration Theory

Hydration is defined as the chemical reaction between water and cement. The four clinker compounds named, tricalcium silicate (C₃S), dicalcium silicate(C₂S), tricalcium aluminate(C₃A) and tetracalcium aluminoferrite(C₄AF) are primarily responsible for hydration process. When cement is mixed with water, cementing compounds of calcium-silicate-hydrate (CSH) and calcium-aluminate-hydrate (CAH) are formed and excess calcium hydroxide is released (Little et al. 2000). Heat is evolved during the process of cement hydration due to breaking and making of chemical bonds.

As seen in the Equations 2.1 and 2.2, C₃S and C₂S react with water in the similar way and produce calcium silicate hydrate and calcium hydroxide.

\[
\begin{align*}
2C_3S + 7H & \rightarrow C_3S_2H_8 + 3CH \quad \text{[Equation 2.1]} \\
\text{(Tricalcium silicate) + (Water)} & \rightarrow \text{(CSH) + (Calcium hydroxide)} \\
2C_2S + 5H & \rightarrow C_3S_2H_8 + 3CH \quad \text{[Equation 2.2]} \\
\text{(Dicalcium silicate) + (Water)} & \rightarrow \text{(CSH) + (Calcium hydroxide)}
\end{align*}
\]
In the process of S/S of soils with cement, some calcium is available to modify the soil particles in the early stage when the water is added and additional calcium becomes available in later stage as a result of cement hydration (Prusinski and Bhattacharja 1997). The hydration reactions and strength gain occurs mostly between 24 hours and 28 days although cement continues to hydrate at slow rate until the free moisture is present (Prusinski and Bhattacharja 1999). Hydrated cements and concrete change their physical properties over time; in a similar way waste treated by cement-based S/S is expected to change the properties in long run (Klitch et al. 1999). Slower hydration kinetics is observed in a material containing portland cement and pozzolanic materials (Bachelor 2006).

**2.2.3 Stabilization/Solidification Application**

The U.S. EPA has identified S/S treatment as the Best Demonstrated Available Treatment Technology (BDAT) for many Resource Conservation and Recovery Act (RCRA) hazardous wastes (PCA 2004). It is most frequently applied treatment technology at Superfund sites in the United States. Over 25% of selected remedies for these sites include the use of S/S contaminated soils and sediments (US EPA 2004). In general S/S treatment technology involves use of the reagents such as portland cement, lime, and pozzolans (fly ash, cement klin dust). S/S treatment technology can be applied to industrial waste, to contaminated soils, sediments or sludge at remediation sites. S/S can be applied to different sites contaminated by heavy metals, PCBs, oils etc. S/S can be
performed ex-situ or in-situ. Figure 2.2-1 and Figure 2.2-2 illustrate the in-situ and ex-situ S/S treatment.

Figure 2.2-1: Solidification/Stabilization - In-situ treatment (USACE EM 1110-1-4007)

Figure 2.2-2: Solidification/Stabilization - Ex-situ treatment (USACE EM 1110-1-4007)

S/S treatment has been successfully applied to Brownfields, Superfund sites, radioactive waste, federal facilities (other than EPA). An example of a
successful sediment S/S occurred at the Brownfield reuse of New York harbor sediment (Wilk 2008). The federal regulations restricted disposal of sediments dredged from the harbors of New York and Newark into ocean. For the treatment of this millions of cubic meters of the dredged sediments the New York port authority adopted portland cement based solidification/stabilization treatment (Douglas et al. 2004). The portland cement based S/S treatment altered the dredged sediments into valuable structural fill. The treated dredged sediments were used to cover 20 acre of landfill which was redeveloped for construction of a shopping mall and 160 acre site was designated for Brownfields redevelopment (SRWCB 2000). Solidification/stabilization of mildly contaminated dredged sediments with cement used as a binder will allow them to be used beneficially. The results of S/S treatment depend on the degree of carbonation of cementitious material present in cement and in sediments.

2.3 Carbonation

It is generally believed that the industrial activities have increased the concentration of CO$_2$ in the atmosphere. The total amount of CO$_2$ released worldwide every year is 7.0 Gton of which 5.4 Gton is caused by use of fossil fuels (Liu et al. 2000b). The causes and effects of increased CO$_2$ have been studied by different scientists for years. There are three main approaches available to reduce the amount of CO$_2$ emitted in the atmosphere: improvement of energy efficiency, use of renewable energy resources and carbon sequestration. The ultimate goal of carbon sequestration is to capture CO$_2$ in a
way to prevent its emission back to atmosphere (Huijgen and Comans 2003).

Simons et al. studied the process of carbon sequestration in artificial construction aggregates, through the carbonation of MSW ashes. (Simon et al. 2003).

Carbonation has been used for the treatment of contaminated soils and different forms of waste materials. Carbonation has been demonstrated to act positively in the immobilization of hazardous wastes contaminated with heavy metals by the process of stabilization/solidification. Solidification of radionuclides using carbonation technique results in precipitation of calcite which significantly affects the mass transportation of cations, by resulting in physical and chemical changes in the material (Smith and Walton 1991).

2.3.1 Accelerated Carbonation

2.3.1.1 Introduction and background –

Lange et al. (1996) observed that in the presence of carbon dioxide the hydration process of cement is accelerated. Accelerated carbonation is the controlled version of natural carbonation process. Accelerated carbonation is the intentional application of CO$_2$ which promotes rapid stiffening of green products along with binding of toxic metals. In the process of accelerated carbonation, the CO$_2$ uptake is high as compared to conventional methods so the percentage of CaCO$_3$ increases (Barnard et al. 2005). Accelerated carbonation activates portland cement to rapidly increase the rate of hydration of calcium silicate phases (Berger et al. 1972).
The kinetics of carbonation reaction of portland cement involve the following detailed reaction steps for $\text{C}_3\text{S}$ and similarly for $\text{C}_2\text{S}$ (Maries 1992). Figure 2.3-1 shows step by step accelerated carbonation reaction in which solid arrows represent instantaneous reactions and hollow arrows represent secondary delayed reaction (Maries 1992).

1 Diffusion of $\text{CO}_2(\text{g})$ in air
2 Penetration of $\text{CO}_2(\text{g})$ through the solid material
3 Conversion of $\text{CO}_2(\text{g})$ to $\text{CO}_2(\text{aq})$
4 Hydration of $\text{CO}_2(\text{aq})$ to $\text{H}_2\text{CO}_3$
5 Ionization of $\text{H}_2\text{CO}_3$ to $\text{H}^+$, $\text{HCO}_3^-$, $\text{CO}_3^{2-}$
6 Dissolution of cement phases
7 Nucleation of $\text{CaCO}_3$, CSH
2.3.1.2 Factors affecting accelerated carbonation -

The extent of carbonation and strength gain depends on the several factors like water content, binder content, time of carbonation, permeability and porosity of the material, temperature and concentration of CO₂.

The rate of CO₂ uptake depends on the water content of the material during accelerated carbonation reaction, with different materials having different optimum water contents for maximum carbonation (Johnson 2000; Fernandez Bertos et al. 2004). Sufficient water is required for the reaction to take place; on the other hand too much water can reduce the diffusion of CO₂ in the material (Young et al. 1974, Lange et al. 1996c). Excess water content delays the reaction. In the material treated with binder, as the binder content increases, the optimum value of water content decreases and water content becomes more crucial in the process of CO₂ uptake (Barnard et al. 2005). The variation in the results of water content is also attributed to the amount of silt/clay present in the material and difficulty in mixing water uniformly in the sample.

Depending on the type of binder, the amount of binder content is optimized in the process of carbonation. It has been identified that there is a non-proportional increases in the CO₂ uptake with increasing binder content (Barnard et al. 2005). The rate of reaction increase with the time of carbonation during initial reaction phase thereafter may decrease as the reaction progresses (Bukowski and Berger 1979). The study carried out by Berger and Klemm
suggested that if the supply of carbon dioxide is stopped before the complete carbonation, normal hydration process will continue resulting in the further strength gain (Berger and Klemm 1972).

Accelerated carbonation is most effective under a 100% CO$_2$ atmosphere. Decrease in CO$_2$ atmosphere decelerates the carbonation reaction significantly (Johnson 2000; Maries 1992, Barnard et al. 2005).

**2.3.1.3 Benefits of accelerated carbonation**

Barnard and Hills studied the benefits of accelerated carbonation over conventional S/S treatment and found that material treated with accelerated carbonation show reduction in pH by 3 or more units compared to material treated with traditional S/S treatment (Barnard et al. 2005). This reduction in pH is caused by formation of carbonic acid (H$_2$CO$_3$) and then ionization to H$^+$, HCO$_3^-$, CO$_3^{2-}$ (Step 5) (Berger et al. 1972). Accelerated carbonation efficiently activates poorly hydraulic cementitious materials such as C$_2$S and calcareous waste (Bukowski and Berger 1979; Maries 1992; Johnson 2000). Another advantage of accelerated carbonation over traditional carbonation technique is high early strength. The rapid reaction of calcium silicate phases of portland cement in accelerated carbonation results in high early strength gain as compared to normal hydration reaction in which strength gain process is prolonged for long period (Maries 1992). The major strength is produced within first few hours of reaction during accelerated carbonation. Whereas, in normal hydration process, strength development in the material takes days (major strength is developed between 24 hours and 28 days). A strong relationship has been established
between the compressive strength and mass of CO$_2$ utilized during the carbonation process (Lange et al. 1996a; Young et al. 1974). In the process of accelerated carbonation of waste material, strength development is predominantly influenced by CO$_2$ uptake and extent of carbonate products produced (Barnard et al. 2005). Accelerated carbonation not only enhances the physical and environmental properties of waste materials for reuse but also upgrade the waste material which is usually disposed in landfill by reducing volume of waste. This is particularly beneficial for those countries where space and capacity of landfills are major issues (Scuzzarella 2004).

L. C. Lange studied the effect of accelerated carbonation on the leaching behavior of waste and found that the carbonated waste forms show significant improvement in metal fixation characteristics (Lange et al. 1996).

2.3.1.4 Application of Accelerated Carbonation -

Accelerated carbonation technique is being utilized to treat different types of waste. The preliminary studies and applications of this method were started in the UK and is now popular worldwide due to its benefits. In the United States, application of accelerated carbonation technique is still under investigation and is used on the laboratory scale. Table 2.3-1 shows all the different forms of waste treated by carbonation technique and their disposal methods.
Table 2.3-1: Wastes treated by carbonation and their usual routes
(Fernández Bertos et. al., 2004)

<table>
<thead>
<tr>
<th>Waste</th>
<th>Usual disposal routes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blast furnace slag</td>
<td>Aggregate manufacturing</td>
</tr>
<tr>
<td>Steel slag</td>
<td>Cement production and concrete admixtures</td>
</tr>
<tr>
<td>MSWI ash</td>
<td>Disposed of in landfill. Incorporated in construction material</td>
</tr>
<tr>
<td>Pulverized fly ash</td>
<td>Additive in building industry</td>
</tr>
<tr>
<td>Sewage sludge ash</td>
<td>Landfilled, concrete production, mineral filler and soil conditioner</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>Stabilization with cement</td>
</tr>
<tr>
<td>Cement kiln dust</td>
<td>Landfilled, agricultural application</td>
</tr>
<tr>
<td>Coal fly ash</td>
<td>Cement products and landfilled</td>
</tr>
<tr>
<td>Foundry sand</td>
<td>Partly reused and partly landfilled</td>
</tr>
<tr>
<td>Blast furnace flue dust</td>
<td>Partly reused and partly landfilled</td>
</tr>
</tbody>
</table>

Many countries in the world are using accelerated carbonation technique to treat waste for improvement in physical properties of waste and/or to reduce leaching potential of the waste. Literature has shown an extensive research and application of accelerated carbonation technique carried out in UK. The effect of carbonation on pH dependent leaching of MSWI bottom was studied by Brouwer et al. in the Netherlands (Brouwer et al. 2006). The research was held at the landfill in Austria where the landfill gas accelerated the in-situ carbonation of MSWI bottom ash (Mostbauer and Lechner 2006). Carbonation treatment method was utilized for recycling of municipal solid waste incinerators residues (MSWIR) as construction material and for stabilization of heavy metals in Japan by Etoh et al., (Etoh et al. 2006). Carbonation treatment in an actual incineration
facility was conducted by S. Sakita in Japan (Sakita et al. 2006). In Belgium, Cizer et al. studied the effect of carbonation on lime mortars where lime hydrate, hydraulic lime and lime with pozzolans are used as binders (Cizer et al. 2006). Also, Thomas Van Gerven and his team from Belgium studied the influence of degree of carbonation on leaching from cement-bound waste (Van Gerven et. at. 2006). There has been some work done in United States on accelerated carbonation but is in the preliminary stages. All the above mentioned examples illustrate the significant potential in the accelerated carbonation technique. It was interested to note that accelerated carbonation was used successfully to treat wide variety of wastes; however accelerated carbonation technique was not used to treat contaminated sediments so far. Finding an appropriate treatment method is crucial to the success of beneficial reuse of mildly contaminated sediments. Section 2.4.1 discussed the advantages of accelerated carbonation technique to treat different waste materials. This research was formulated to design and examine the performance of mildly contaminated sediments treated by accelerated carbonation technology. The design and optimization of materials and methods used in this research is thoroughly discussed in Chapter 3.
CHAPTER 3

MATERIALS AND METHODS

This chapter describes the different materials and methods used to produce artificial aggregates, along with the analysis methods used to characterize the aggregates. This chapter is divided into four sections. The first section describes the properties of the materials used in this research. The second section describes the procedures used for production of artificial aggregates in small scale experimentations. The full scale production of the artificial aggregates using mini concrete mixer is covered in the third section. The final section describes the methods of analysis used to characterize the mechanical/physical and environmental properties of the aggregates.

3.1 Components of Artificial Aggregates

The basic components used to produce the artificial aggregates were dredged sediments, binder, water and carbon dioxide. Their relevant physical and environmental properties are summarized in this section.

3.1.1 Dredged Sediments

The aim of this research was to develop a process to produce artificial aggregates using mildly contaminated sediments. This process was based on
optimization of the mix proportions and optimization of the methods. Hence, numerous trials were made. Considering the risks of using a large volume of contaminated sediments from a disposal and handling point of view, it was decided to use clean sediments for the mixture design work. Contaminated sediments were used for leaching tests after the mixture design experiments were complete. The clean sediments were collected from Great Bay, New Hampshire. The contaminated sediments were collected from the Gowanus Canal, Brooklyn, New York.

The Great Bay (GB) sediments were grayish brown in color and had a stringent odor (Figure 3.1-1). The natural water content of these sediments was 55 % ± 1.5 %. Specific gravity of Great Bay sediments was approximately 2.69. Specific gravity testing was done in accordance with ASTM D 854-00 method A. The Liquid limit was 61 % ± 2 % and Plastic limit was 35 % ± 2 %. The organic content for Great Bay sediments was found out using LOI method (ASTM D 2974-00).

![Figure 3.1-1: Dredged Great Bay sediments in 5 gallon bucket](image-url)
An oxide analysis of Great Bay sediments was adopted from William Nourse (Nourse 2005). Table shows results of sediment oxide analysis.

Table 3.1-1: Great Bay sediment oxide analysis

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>66.61</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.30</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.87</td>
</tr>
<tr>
<td>CaO</td>
<td>1.76</td>
</tr>
<tr>
<td>MgO</td>
<td>1.29</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.34</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.03</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.56</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.71</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.18</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0.06</td>
</tr>
<tr>
<td>SrO</td>
<td>0.03</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.02</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.01</td>
</tr>
<tr>
<td>Water Content</td>
<td>0.02</td>
</tr>
<tr>
<td>LOI (950°C)</td>
<td>6.64</td>
</tr>
<tr>
<td>Total</td>
<td>99.43</td>
</tr>
</tbody>
</table>

The received GB sediments had high water content (55%). For simplicity in the experiments and to have better control over the percentage of water in the mixture, it was decided to use dry sediments. The sediments were air dried in the sun on geotextile fabrics (Figure 3.1-2). Lumps of dried sediments were formed due to the presence of clay. These lumps were broken down into smaller
fractions. The sediments were then sieved through 425 micron sieve (#40 mesh) to remove small rocks, shells, wood pieces and litter. According to William Nourse's work (2005), it was clear that most material passes the #40 mesh, hence the sieving was mostly for removing debris.

![Figure 3.1-2: Atmospheric drying of dredged sediments on 3' x 3' geotextile stand](image)

As mentioned earlier, clean Great Bay sediments were used in the preliminary experiments to reduce the risks involved. However, it was necessary to use contaminated sediments to evaluate the performance of the artificial aggregates in terms of leaching after the accelerated carbonation treatment. For this purpose contaminated sediments with high percentage of heavy metals from Gowanus Canal, NY were used. The total available metal content for release of Gowanus canal (GC) sediments compared to NIST values is shown in Table
3.1-2. NIST is the National Institute of Standards and Technology whose standard reference material (SRM 1646a) program is used for evaluating the analytical methods for the determination of the trace elements in estuarine sediments (Standard Reference Material 1646a). NIST values are used as a comparison to show the natural metal levels in sediments, hence as per Table 3.1-2, metal concentrations in Gowanus Canal sediments are significantly higher.

The USEPA Toxicity Characteristic Leaching Procedure (TCLP) was used to evaluate leaching of metals under specific environmental scenarios such as leaching of constituents into the groundwater from landfills (Tsiatsios 2005). The solid content and organic content of sediments were also determined. For determination of solid fraction, sediments were dried at 103°C-105°C (ASTM D 2974-00). Organic content was determined using Loss on Ignition method (ASTM D 2974-00). The solid fraction in Gowanus canal sediments was 41 % and LOI was 5.7 % (Adapted from Christopher James Tsiatsios 2005).

<table>
<thead>
<tr>
<th>Constituent</th>
<th>NIST (SRM 1646a)</th>
<th>Gowanus Canal (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>6.23</td>
<td>8.5</td>
</tr>
<tr>
<td>Cd</td>
<td>0.148</td>
<td>4.4</td>
</tr>
<tr>
<td>Cr</td>
<td>40.9</td>
<td>75</td>
</tr>
<tr>
<td>Cu</td>
<td>10.01</td>
<td>240</td>
</tr>
<tr>
<td>Ni</td>
<td>23</td>
<td>30</td>
</tr>
<tr>
<td>Pb</td>
<td>11.7</td>
<td>250</td>
</tr>
<tr>
<td>Zn</td>
<td>48.9</td>
<td>330</td>
</tr>
</tbody>
</table>

(Adapted from Christopher James Tsiatsios 2005)
3.1.2 Binder

The binder plays an important role in the production of artificial aggregates. The importance of binder in the process of accelerated carbonation was discussed in Chapter 2. The carbonation reaction requires CaO, MgO, Ca(OH)$_2$ to be present in the binder material. There are a number of potential binders: portland cement, coal fly ash, lime, cement kiln dust etc. In this research, portland cement was used as the binder, as it was readily available and it has been used successfully in the traditional S/S treatment of waste previously in many studies, which provides a reference for the effectiveness of accelerated carbonation. The selection of cement in the process of S/S treatment is discussed in details in Chapter 2.

Type II portland cement was used in the experiments. The portland cement was stored in 5 gallon buckets and care was taken to keep the cement away from any possible exposure to moisture. The results of chemical analysis of the Type II portland cement sample, (adapted from William Nourse 2005) were in accordance to ASTM C 150-02a and are shown in Table 3.1-3 and Table 3.1-4. According to ASTM C 150-02, in Type II portland cement the percentage of (C$_3$S+ C$_3$A) shall not exceed 58 %. Type II portland cement has moderate heat of hydration. This type of cement has resistance to sulfate attack and usually it is used when material is in contact with soils and ground water.
Table 3.1-3: Compound percentages of portland cement type II

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight %</th>
<th>ASTM C 150-02 (Type II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>51.0</td>
<td>C₃S+C₃A = 58.0 %, max</td>
</tr>
<tr>
<td>C₂S</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>C₃A</td>
<td>7.0</td>
<td>C₃A = 8.0 %, max</td>
</tr>
<tr>
<td>C₄AF</td>
<td>10.0</td>
<td></td>
</tr>
</tbody>
</table>

(Adapted from William Nourse 2005)

C₃S – Tricalcium silicate
C₂S – Dicalcium silicate
C₃A – Tricalcium aluminate
C₄AF – Tetracalcium aluminoferrite

Table 3.1-4 Oxide percentages of portland cement type II

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight %</th>
<th>ASTM C 150-02 (Type II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>20.28</td>
<td>20.0 %, max</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.58</td>
<td>6.0 %, max</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.13</td>
<td>6.0 %, max</td>
</tr>
<tr>
<td>CaO</td>
<td>61.32</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>3.58</td>
<td>6.0 %, max</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.27</td>
<td>3.0 %, max</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>SrO</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>LOI (950°C)</td>
<td>1.90</td>
<td>3.0 %, max</td>
</tr>
<tr>
<td>Total</td>
<td>100.13</td>
<td></td>
</tr>
</tbody>
</table>

(Adapted from William Nourse 2005)
3.1.3 Water

Water used in this research was regular Durham, NH tap water. pH of tap water was around 7.2-7.7 (AWWA Research Foundation, 1999). No special treatment was used on the water.

3.1.4 Carbon Dioxide

Industrial grade carbon dioxide was used for carbonation of the samples, supplied in a high pressure gas cylinder. Two carbon dioxide cylinders were used during total research period which were supplied by same vendor. The density of carbon dioxide is 1.98 kg/m$^3$ which is about 1.65 times that of air, an important factor in the mixing process.

3.2 Small Scale Experimentation

In this section different techniques used for the carbonation of the mixture are described. The first subsection describes different methods for exposing the sediment-binder mixture to CO$_2$. The second subsection describes studies of carbonation with respect to time. This subsection includes continuous and cyclic carbonation. Experiments were also carried out to determine the optimum time required for the material for maximum amount of carbonation.

3.2.1 Method of Carbonation with respect to Mechanism

This subsection explains the different techniques used for carbonation of the sediment-binder mixture. Three types of techniques were applied. The aggregates were carbonated in a stand mixer, in columns and in a tumbler.
3.2.1.1 Mixer -

In these experiments the mixture was carbonated in a stand mixer. While sediments, portland cement and water were being mixed, carbon dioxide was supplied in the mixer. To maintain the carbon dioxide around the mixture, the container of the stand mixer was covered with a plastic sheet. The plastic sheeting was punctured so as to pass a tube supplying carbon dioxide. Figure 3.2-1 shows the experimental arrangement adapted.

These experiments were performed at an early stage of research so different trials were done to optimize the method. At first water was added slowly to the dry sediments. Once the water and sediments were thoroughly mixed, a known quantity of portland cement was added to the mixture. In this process, portland cement was not uniformly distributed all over the mixture because lumps of sediments were formed immediately after adding water.

Subsequently, sediments and portland cement were dry mixed in the stand mixer and then the water was added gradually. Total weight of the dry materials in the mixture was restricted to 1000g. Different trials were made with various mix proportions of sediments and portland cement, and water was added gradually with the increments of 10g until the small aggregates were formed. While all the ingredients were being mixed carbon dioxide was introduced. It was observed that dry mixing of portland cement and sediments enable uniform mixture formation. The main purpose of mixing is to achieve a homogeneous mixture of all the components (Chang and Peng 2001). The mixing process was working well, so all the samples after preliminary experimentation were made
using this method of mixing. However, it was critical to develop another method for carbonating the mixture.

![Static carbonation set up in stand mixer](image)

**Figure 3.2-1: Static carbonation set up in stand mixer**

The challenge in the process of carbonation was, being an exothermic reaction that the temperature was raised and water was liberated during the reaction and the mixture became too wet. Also, while adding water gradually, lifting of plastic sheet cover caused loss of \( \text{CO}_2 \). This did not ensure 100% \( \text{CO}_2 \) atmosphere in the process of accelerated carbonation. Hence, keeping the method of mixing unchanged, new method of carbonation was developed called 'column carbonation'.

**3.2.1.2 Column -**

A column with 2.5 cm internal diameter and 20 cm in length was used to carbonate the samples. The sediments and portland cement were dry mixed and water was added gradually. In the method of column carbonation, sediments,
Portland cement and water were mixed in stand mixer beforehand and then carbonated. Considering a small volume (491 cm$^3$) of column, less mixture was prepared in the stand mixer. The total weight of mixture was limited to 500g to limit the material wastage. Unlike previous experiments, the total weight of all the three components together was kept constant with different mix proportions of Portland cement, sediments and water. The results are discussed in detail later in Chapter 4.

![Column carbonation set up](image)

**Figure 3.2-2: Column carbonation set up**

In each test, 20 grams of material was placed in the column. Two flow meters, one with a capacity of 1 L/min at the inlet and other with a capacity of 6 L/min at the outlet of the column were attached to monitor the flow of carbon dioxide. The flow rate was maintained between 0.8 L/min and 1 L/min. Carbon dioxide is mixed with water in the water bath and then passed through the column for carbonation.
dioxide was passed through a water bath to maintain a high relative humidity. 
Samples were carbonated typically for 2 hours.

3.2.1.3 Tumbler -

A tumbler was custom made in accordance with the requirements of the 
experiments. A wooden disc was made in a way so that 16 bottles could be 
mounted on the disc at a time (Figure 3.2-3). The disc rotated about a hollow 
copper pipe which was connected to a motor. The motor rotated at a speed of 
30-35 rpm. Perforations were made in the copper pipe through which plastic 
tubes were attached. Each plastic tube was connected to bottle. Two holes were 
drilled through cap of each bottle, one for attaching the carbon dioxide supply 
tube in the bottle and other for getting carbon dioxide out of bottle so that 
pressure in the bottle remain near atmospheric. This was necessary as with no 
hole, within first half hour bottles were swollen.

Figure 3.2-3 : Tumbler set up
20g of sample was placed inside each bottle. The sample was prepared in the stand mixer with different mix proportions of sediments, portland cement and water. The method of sample preparation is explained in section 3.2.1.1. Optimization of the process and analysis for the characterization of artificial aggregates was done using the samples carbonated in tumbler. Using tumbler for the carbonation, carbon dioxide was mixed thoroughly with aggregates. Also, performing the experiments on several samples at once was possible because of the capacity of tumbler to mount 16 bottles at a time.

### 3.2.2 Methods of Carbonation with respect to Time

As carbonation is the important process in making artificial aggregates, samples were carbonated using two methods: continuous carbonation and cyclic carbonation. Having an appropriate mixture sequence and adequate mixing time are crucial to develop uniformity throughout the mixture. This in turn has an impact on the performance characteristics of the cementious material (Vandanjon et al. 2003). As discussed in Chapter 2, the percentage of reacted material will increase with time of carbonation (Bukowski and Berger 1979).

#### 3.2.2.1 Continuous carbonation -

In this method samples were carbonated continuously for a set of time period. The materials were mixed in a stand mixer and were placed in a tumbler for carbonation. Carbon dioxide was continuously supplied passing through material. Ten bottles carrying mixture were mounted on a tumbler. Two bottles were removed from the tumbler after every hour. Samples were collected every
hour for a total period of five hours. All the samples were analyzed for its CO₂ uptake. Figure 3.2-4 shows representative samples collected from bottles.

![Samples collected from tumbler](image)

**Figure 3.2-4: Samples collected from tumbler**

### 3.2.2.2 Cyclic carbonation -

In cyclic carbonation, the samples were carbonated in one hour cycles. At first, aggregates were made and were carbonated in the tumbler for an hour. After initial one hour carbonation, the samples were dried in an oven at 100°C for 2 hours. Samples were brought to room temperature by placing them in desiccator. The samples were ground to powder and were weighed. Water was added to the dry sample to bring the water content back to the initial value. The mixture was uniformly mixed and was placed in the tumbler for the next round of one hour carbonation. The same procedure was repeated for every cycle of carbonation. This procedure was adopted to evaluate performance of continuous carbonation against cyclic carbonation. Figure 3.2-5 shows sample kept in
desiccator. Samples were carbonated for total three hours i.e. 3 cycles of carbonation. The time was limited to three hours as it was seen that maximum CO$_2$ uptake takes place within first two hours of carbonation. Results are discussed in Chapter 4.

![Samples in desiccator](image)

**Figure 3.2-5: Samples in desiccator**

### 3.2.2.3 Method to determine time of carbonation

To obtain the optimum time of carbonation, a sample was carbonated for 5 hours. The same method of continuous carbonation explained in Section 3.2.2.1 was adopted in this process. After each hour of carbonation a small amount of sample was taken out for analyzing CaCO$_3$ content.

### 3.3 Full Scale Experimentation - Method of Carbonation and Mixing

In previous section small scale experiments were explained. Small scale experiments were performed for the optimization of process and key parameters.
However, the size and output of material produced was limited by the scale of the experiments. Full scale experiments were performed with the optimum mixture. The artificial aggregates were created and were analyzed for its physical properties. The stability of contaminants in the aggregates was checked using pH dependent leaching.

For the production of artificial aggregates on the full scale, a Red Lion 636001 Big Cat mini concrete mixer was used. The concrete mixer, as seen in Figure 3.8, has a 3.5 ft³ drum which could be positioned at an angle. The drum had an outer diameter of 32 inches and contained 3 blades. According to the requirements of experimentation some modifications were carried out. Figure 3.3-1 shows detail set-up of full scale experiments.

A wooden circular lid was made to cover the drum of the concrete mixer. A hole was drilled through the wood and a small PVC pipe was inserted. Two Teflon tubes were passed through the PVC pipe. One Teflon tube carried water into the drum and another carried carbon dioxide. A small valve was attached to the water supply tube to control the flow of water into drum. At the end of water supply tube a small bottle with perforations was attached which acted as a sprinkler. A water container with tap was used as a water tank and a known quantity of water was placed in it beforehand. A cylinder of industrial grade carbon dioxide was used to carbonate the aggregates.

A known amount of sediments were poured in drum. Considering the mix proportion, portland cement was then added to sediments. Table 3.3-1 shows the weight and percentage of each component used.
Table 3.3-1 Mix proportion used for sample preparation

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (grams)</th>
<th>% contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediments</td>
<td>8250</td>
<td>55</td>
</tr>
<tr>
<td>Portland Cement</td>
<td>3750</td>
<td>25</td>
</tr>
<tr>
<td>Water</td>
<td>3000</td>
<td>20</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>15000</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

![Figure 3.3-1: Mini concrete mixer with modification](image)

Dry mixing was carried out for 10 minutes. A uniform dry mixture was obtained as the drum revolved. Using the control valve water was added to the dry mixture gradually. With the help of perforated bottle attached at the end of water supply tube, water was sprinkled uniformly throughout mixture. Using this set-up all the three components of artificial aggregates were mixed uniformly.
while carbonation was in progress. Carbonation was carried out for 2 hours. After completion of carbonation, the temperature was measured using a thermometer and sample was collected for water content.

3.4 Method of Analysis - Characterization of Artificial Aggregates

The ultimate goal of this research was to obtain solidified and stabilized artificial aggregates. According to literature covered in Chapter 2, accelerated carbonation helps to enhance the strength of material along with enhancing the metal retention properties of the material. To check the degree of carbonation i.e. CO₂ uptake during the formation of calcium carbonate, different techniques were used. Thermal techniques like Thermo Gravimetric Analysis (TGA) and Loss on Ignition methods were applied. The details of TGA are discussed in section 3.5. These methods were used to analyze the aggregates made in small scale experiments for optimizing the process parameters and key parameters.

The results from small scale experiments initiated the selection of optimum mix proportion from the total experimental region. The design of experiments and statistical analysis methods used are covered later in this chapter. The full scale production of aggregates was performed using mini concrete mixer. These aggregates were analyzed for their physical properties and leaching behavior using different techniques. This section describes the methods of analysis used for the characterization of the aggregates and optimization of the process.
3.4.1 Water Content

The natural water content of dredged sediments as well as artificial aggregates was determined. An empty container was weighed. Samples were placed in the container and weighed again. Samples were heated in oven at 100°C. After 24 hours, the dry samples were weighed. By subtracting the weight of empty container, the dry weight and wet weight of the samples was determined. Typically, water contents of four samples were determined and the average was obtained. The water content was calculated using the equation given below.

Water content (%) = \( \frac{W_w}{W_s} \times 100 \)  

[Equation 3.1]

Where:  
\( W_w \) = weight of water (grams)  
\( W_s \) = weight of solids (grams)

3.4.2 Sieve analysis

The particle size distribution of aggregates was determined using sieve analysis (AASHTO T 27-99). Aggregates were air dried before passing through set of sieves. Aggregates weighing 9 kg were sieved using mechanical sieve shaker. Sieves were arranged starting with 100 mm sieve and gradually descending with the smallest sieve of 0.075 mm opening. The actual set of sieves used for determining particle size distribution was 100 mm, 76.1 mm, 64 mm, 50.8 mm, 37.7 mm, 25 mm, 19 mm, 12.5 mm, 9.5 mm, 4.75 mm, 2 mm,
0.425 mm, and 0.075 mm. Sieve analysis was particularly important to decide the gradation of aggregates.

### 3.4.3 Atterberg Limits

Determination of Atterberg limit is important for degree of firmness i.e. consistency. This term is mostly used for fine grained material. It was decided to perform Atterberg tests on the Great Bay sediments as they contained high percentage of fines and have high natural water content. The Atterberg limits or consistency limits are the water contents at which a soil mass (here sediments-cement mixture) passes from one state to another. These different states, namely: solid state, semi-solid state, plastic state and liquid state are drawn from the behavior of a soil mass at different water contents. The Atterberg limits which are mostly used for geotechnical purposes are the liquid limit and plastic limit.

The liquid limit is the water content at which material is still in liquid state however it has a small shearing resistance against flowing. This can be determined using Casagrande’s apparatus. The plastic limit is the water content at which soil begin to crumble when rolled into thread of approximately 3 mm diameter. The range between liquid limit and plastic limit is called ‘Plasticity Index’.

\[
\text{PI} = \text{LL} - \text{PL} \\
\text{[Equation 3.2]}
\]

Where:

- PI = Plasticity Index
- LL = Liquid Limit (%)
- PL = Plastic Limit (%)
Plotting plasticity index against liquid limit helps to determine the type and physical properties of soil/material. A-line is the empirical line showing separation between cohesive and non-cohesive soils (Figure 3.4-1).

Figure 3.4-1: Casagrande’s plasticity chart

3.4.4 Loss on Ignition (LOI)

Loss on ignition was performed on raw sediments to determine the organic content and carbonate content. LOI was conducted on carbonated sediments and carbonated aggregates as well. Around 5-6 samples were run and an average of all the samples was taken. To compare the results of LOI and TGA, samples were heated in a nitrogen controlled atmosphere in a muffle furnace.
A muffle furnace manufactured by Barnstead/Thermolyne was used (Figure 3.4-2). The furnace was capable of heating sample up to 1100°C. The porcelain crucibles of 15 gm capacity were used as a sample pan. Samples were heated in three steps:

1. Samples were heated till 105°C and the temperature was held for 12 hours.
2. Samples were heated till 550°C and the temperature was held for 2 hours.
3. Samples were heated till 950°C and the temperature was held for 2 hours.

The heating rate was kept constant at 20°C/min. Weight loss for all three ranges was determined. Organic content of sample was obtained between 105°C and 550°C. Carbonate content of sample was obtained between 550°C and 950°C.
3.4.5 Modified Proctor Test

The modified Proctor test was used to determine the degree of compaction. Compaction is a process by which soil particles are arranged in a way to decrease the porosity thus increasing its dry density. Modified proctor test was developed for higher standard of compaction. The modified proctor test was performed according to AASHTO T 180-01. In this test soil/material was compacted in Standard Proctor mold. Material was compacted in 5 layers, each layer being given 25 blows of 10 lb (4.89 kg) rammer from a drop of 18 inches (45 cm). A plot of dry density against water content was plotted to give the maximum dry density for optimum water content.

3.4.6 California Bearing Ratio (CBR)

CBR test is a penetration test which is performed to evaluate the strength of laboratory compacted material. This method is applicable to the material used for pavement subgrade, subbase, and/or base/course. CBR testing was done according to AASHTO T 193-99. CBR compares the bearing capacity of the material with that of a well graded crushed stone (which should have CBR ~ 100 %). CBR may be determined at optimum moisture content hence the results from Proctor test were useful in performing CBR. The CBR number is found as a percent of corrected load divided by the standard load each 0.1 inch (1000 psi) and 0.2 inch (1500 psi) deflections. The CBR numbers were calculated using Equation 3.3.

\[
CBR (\%) = \left( \frac{P_c}{P_s} \right) \times 100
\]  

[Equation 3.3]
Where: \[ P_c = \text{Corrected Load Value} \]

for 2.54 mm (0.1") or 5.08 mm (0.2") of penetration

\[ P_s = \text{Standard Load Value} \]

Type of material and suitability of material in subgrade and/or subbase is decided by comparing the CBR value of material with standards.

### 3.5 Thermo gravimetric Analysis (TGA)

Thermo Gravimetric Analysis (TGA) was used to measure the change in mass of a material as a function of temperature and/or time, under controlled atmosphere. Here a nitrogen controlled atmosphere was used. In TGA, decomposition of free water, decomposition of chemically bound water and evolution of carbon dioxide is determined, which indicated the presence of calcium hydroxide \( \text{Ca(OH)}_2 \) and calcium carbonate \( \text{CaCO}_3 \). A sample pan of very small size, approximately 5 mm diameter, was used to carry the sample. Approximately 9-13 mg sample was placed in a tared sample pan. A sensitive microbalance assembly helped to calculate weight change of sample in reference to the reference pan.
Figure 3.5-1: TGA instrument assembly

The balance assembly measured initial weight of sample at room temperature and then continuously monitored weight change in the sample (loss or gain) with respect to temperature. Software provided with the TGA plotted a graph of weight change with respect to temperature and rate of weight change with respect to temperature. An amount of weight change or percentage of weight change could be obtained for particular range of temperature or at particular temperature. Settings enabled to set the rate of heating and final temperature. The plots for comparison of different samples could be obtained. Figure 3.5-2 shows typical TGA graph for standards Ca(OH)\textsubscript{2} and CaCO\textsubscript{3}. Dotted lines show derivative curve and solid lines show weight change curve. On the derivative curve, blue dotted peak shows decomposition of Ca(OH)\textsubscript{2} between 350°C and 450°C and green dotted peak shows decomposition of CaCO\textsubscript{3} between 600°C and 800°C. Raw sediments, portland cement, different mix
proportions of artificial aggregates and some standards were analyzed using TGA.

![Figure 3.5-2: Typical TGA graph for standards]

**3.5.1 Extent of Carbonation Depth**

The aggregates produced in the concrete mixer were of approximately 2-4 cm in size. The carbonation reaction is diffusion controlled hence it is important to determine the diffusion of carbon dioxide from cover to core of an aggregate. To determine the degree /extent of carbonation with varying sizes of aggregate thermogravimetric analysis (TGA) was performed.

Different size aggregates ranging from 1 cm to 4 cm were selected. These aggregates were cut in half (See Figure 3.5-3). A small amount of sample was
collected from the cover, middle portion and core of an aggregate. The CO₂ uptake i.e. percentage of CaCO₃ was determined using TGA.

Figure 3.5-3 : Whole aggregate (~ 4 cm) and cut into half aggregate

3.5.2 Scanning Electron Microscopy (SEM)

A scanning electron microscopy (SEM) was used to examine the presence of calcium carbonate crystals in artificial aggregates. SEM analysis was performed at the UNH Instrumentation center using an Amray 3300FE field emission SEM with PGT Imix-PC microanalysis system (Figure 3.5-4).

This system was capable of providing three dimensional visual interpretation of the specimen surface. The SEM used electrons instead of light waves to produce images hence the sample was coated with some electricity conductive material. The aggregate sample was coated by gold as atomic weight of gold is much higher than the atomic weight of calcium, oxygen and carbon.

SEM was performed on artificial aggregates produce in the concrete mixer. The average size of these aggregates was approximately greater than 4
cm. To examine the distribution of calcium carbonate throughout the cross-section, a representative aggregate was cut into half. By grinding the circular portion of aggregate with sand paper the thickness was reduced to 2-3 mm. This was necessary as the sample was degassed before procedure started. The greater the thickness, the greater the difficulty, to degas the sample. The upper side was kept normal to see the texture of material. The aggregate was placed on 1 inch diameter metal disc called as stub. To fuse the aggregate on the stub a carbon adhesive was used. Images were captured at center of aggregate moving towards edge of aggregate.

Figure 3.5-4: Amray 3300FE field emission SEM

3.6 Stabilization of Contaminated Sediments - pH Dependent Leaching Test

Analysis of environmental properties such as leaching characteristics is very crucial to determine before application of treated contaminated sediments in
the field. Tests were conducted to evaluate the leaching characteristics (chemical) on both stabilized and non-stabilized sediments. Generally, different methods are used to evaluate the leaching behaviour of contaminated sediments like pH dependent leaching test, column leaching test, concise leaching test etc (Tsiasios 2005). Since pH is one of the main leachate controlling parameters, the pH dependent leaching test was utilized to provided information on the pH sensitivity of leaching behaviour of the artificial aggregates.

The pH dependent leaching test was performed to investigate the leaching characteristics of the raw sediments as well as of artificial aggregates to ensure the performance after accelerated carbonation treatment applied to contaminated sediments.

Briefly, sample (100 g) was placed in 125 ml Teflon container and were mixed to the liquid to solid ratio (L/S=10) of 10:1. Magnetic stirrers were used to keep the sediments suspended. Sediments were leached for 24 hours. Using the pH static controller and auto burette titrating with HNO₃ or NaOH, pH was kept constant at pH 4, 6, 7, 8, 10, 12. Leachate was vacuum filtered through 0.45 μm nucleopore filter, acidified with 50 μl high purity nitric acid. Samples were stored in vials in refrigerator for analysis in ICP-AES.
3.7 Statistical Methods

The design of experiments approach has been used in industry since the 1940's for all types of experimentation (Snee 1985). Design of experiments (DOE) is a proven statistical tool which has provided improvements in the performance and efficiency of experimentation. The DOE helps in minimizing the required number of tests to reach a valid conclusion. Different methods are used for designing experiments in engineering applications, such as full factorial, fractional factorial and mixture designs. This chapter provides an overview of the mixture type DOE and its application to this work.

3.7.1 Mixture Design

Mixture experiments are best suited for experiments where different materials are mixed together to achieve a specific outcome. For example, different materials are mixed together to create concrete of a specified strength. In mixture designs, constraints can be imposed on the possible settings of each factor. The most important constraint in a mixture experimental design is the sum...
of all the experimental factor settings must be unity. This is shown in Equation 3.4 for a mixture design with ‘q’ factors. The settings of each factor cannot be adjusted independently. From the equation it can be seen that if the amount of one factor is increased, the amount of one or more of the other q-1 factors must be decreased. Each factor may range between 0 and 1.

\[ X_1 + X_2 + \ldots + X_q = 1.0 \quad \text{for} \quad 0 \leq X_i \leq 1.0 \]  

[Equation 3.4]

Where:
- \( q \) = number of factors
- \( i = 1, \ldots, q \)
- \( X_1, X_2, \ldots, X_q \) = amount of factor

Factors may be constrained due to experimental goals, previous research and economic concerns. For each factor range a lower limit and an upper limit may be applied (Snee 1975). As shown in the Equation 3.5, the basic principle of mixture design must be satisfied.

\[ 0 \leq L_i \leq X_i \leq U_i \leq 1.0 \]  

[Equation 3.5]

Where:
- \( L_i \) = lower limit of \( i^{th} \) factor
- \( U_i \) = upper limit of \( i^{th} \) factor

There are several types of mixture designs, including simplex lattice, simplex centroid and the extreme vertices design. When there are no constraints on factors, the simplex lattice and simplex centroid design are most suitable. The extreme vertices design works well for the experimental factors with constraints.
In this research, the amount of water and cement was constrained, so the extreme vertices design with reduced amount of runs was utilized.

### 3.7.2 Experimental Design

The aim of this research was to develop artificial aggregates by using the basic components like sediments, portland cement and water. Experiments were designed to optimize the blending properties of these basic components. Description of each component material is given in Section 3.1. Due to the importance of proportions of each component, it was decided to use a mixture design for this research. The statistical software package JMP® was used to select the optimum experimental points in the mixture space by performing DOE. Since there were three components, the experiments were designed with factors \( q = 3 \). Lower limits and upper limits of all the three components were decided on the basis of preliminary studies and literature.

Water is one of the most important components of this mixture design. As discussed in Chapter 2, an excess amount of water halts the carbonation reaction; on the other hand too little water also halts the carbonation reaction. In the previous studies done on waste treated with binder, the water to solid ratio was restricted from 0.1 to 0.3, with the optimum water content around 12%. Here, the number is a ratio which represents mass of that particular material to the total mass of the mixture. This was taken as starting point in the experiments. Preliminary experiments were performed with varying water content of 10%, 15%, 20%, 25% and 30% in order to determine the constraints. Hence, it was decided to limit the water content between 9% and 30%. Details about the
preliminary experiments are covered earlier in this chapter. Portland cement is another important component in this mixture design. The more the amount of portland cement in the mixture, the better the results. However, it is not feasible from economic point of view to increase the amount of portland cement in the mixture. Also, it was observed in preliminary experimentation that more the quantity of portland cement, bigger the size of aggregate. The goal of this research was to form aggregates and not big chunks or blocks of cement. On the basis of these concerns portland cement was constrained between 7.8% and 30%. One goal of this research was to maximize the amount of sediments in the mixture. Following the basic rule of mixture design (sum of factors is equal to 1, as shown in equation 3.3) the sediment content was restricted between 40% and 82%. Table 3.7-1 shows the lower limits and upper limits for sediments, portland cement and water utilized in mixture design. Component settings are presented in percentages of total mass. The experimental points were selected using the extreme vertices design. From the previous experimentation additional data points were added in the mixture design region.

The extreme vertices design in JMP® generated 18 points for the mixture design. Six points were added manually in order to cover the entire mixture space. Hence, 24 unique points were analyzed. These 24 points were replicated twice in order to account for error. The final mixture design is presented in Table 3.7-2.
Table 3.7-1: Constraints for components in final mixture design

<table>
<thead>
<tr>
<th>Component</th>
<th>Constraints</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lower Bound</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>0.091</td>
</tr>
<tr>
<td>Portland Cement</td>
<td>0.078</td>
</tr>
<tr>
<td>Sediments</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 3.7-2: Final mixture design

<table>
<thead>
<tr>
<th>Mixture ID</th>
<th>Water</th>
<th>Portland Cement</th>
<th>Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.1</td>
<td>18.2</td>
<td>72.7</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>14.5</td>
<td>75.5</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>17.5</td>
<td>72.5</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>25</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>13</td>
<td>17.4</td>
<td>69.6</td>
</tr>
<tr>
<td>8</td>
<td>16</td>
<td>10</td>
<td>74</td>
</tr>
<tr>
<td>9</td>
<td>16.7</td>
<td>16.7</td>
<td>66.7</td>
</tr>
<tr>
<td>10</td>
<td>16.7</td>
<td>20.8</td>
<td>62.5</td>
</tr>
<tr>
<td>11</td>
<td>20</td>
<td>10</td>
<td>70</td>
</tr>
<tr>
<td>12</td>
<td>20</td>
<td>16</td>
<td>64</td>
</tr>
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<td>13</td>
<td>20</td>
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<td>50</td>
</tr>
<tr>
<td>15</td>
<td>21.3</td>
<td>15.7</td>
<td>63</td>
</tr>
<tr>
<td>16</td>
<td>21.9</td>
<td>11.7</td>
<td>66.4</td>
</tr>
<tr>
<td>17</td>
<td>22</td>
<td>19</td>
<td>59</td>
</tr>
<tr>
<td>18</td>
<td>22.5</td>
<td>7.8</td>
<td>69.8</td>
</tr>
<tr>
<td>19</td>
<td>23.1</td>
<td>15.4</td>
<td>61.5</td>
</tr>
<tr>
<td>20</td>
<td>25</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>21</td>
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<td>10</td>
<td>60</td>
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<tr>
<td>22</td>
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<td>55</td>
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<td>30</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>24</td>
<td>30</td>
<td>30</td>
<td>40</td>
</tr>
</tbody>
</table>
The ternary plot in Figure 3.7-1 represents the mixture space that was utilized for the research. As shown in the plot, the mixtures at the vertices of the graph are 'pure component' blends i.e. they are 100% mixture of the single component. The three sides of the graph represent 'binary component' blends i.e. they are the blends of the mixture factors assigned from each adjacent vertices. The mixtures interior to the perimeter of the triangle are blends of all three components. Hence, as seen in the Figure 3.7-1, the points inside the ternary plot are blends of all the 3 components. All the 24 unique points comprise the experimental region. The mix proportions shown in Table 3.6 were evaluated for accelerated carbonation. Details of the carbonation methods are given earlier in this chapter. The thermal analysis was performed to obtain percentage of calcium carbonate.

![Figure 3.7-1: Ternary plot depicting experimental region](image)

Figure 3.7-1: Ternary plot depicting experimental region
CHAPTER 4

RESULTS AND DISCUSSION

This chapter is organized into five sections. The first section deals with the results of studies done to evaluate the material properties that could contribute to viable use of dredged sediments in the production of artificial aggregates. The second section discusses results from small scale experiments for the optimization of key parameters of the carbonation process. The third section addresses statistical analysis and optimization of the results modeling. The forth section is an examination of the optimized mixture. This section includes detailed characterization of material properties and scanning electron microscopy imaging. Finally, results from pH dependent leaching tests are covered in the fifth section.

4.1 Material Evaluation

Characterization of raw sediments was performed to determine the practicality of using dredged sediments in the manufacturing of artificial aggregates. Different physical properties were determined for Great bay sediments. This section covers the results from the studies of natural water content, specific gravity and loss on ignition (LOI) of Great Bay sediments.
4.1.1 Natural Water Content of Great Bay Sediments

The water content of the Great Bay sediments was determined as explained in Chapter 3. The average water content was 55 %, with a standard deviation of 1.5 %. This was the initial water content of the sediments in the drum. As the initial water content was too high for the uniform mixing of binder in the dredged sediments it was decided to use dry sediments to have proper control over the water content of mixture.

4.1.2 Specific Gravity

The specific gravity of the sediments was 2.69. The normal range of specific gravity for natural soils and sediments is between 2.60 and 2.80. Typically it is assumed as 2.65 (USACE (1) 1995).

4.1.3 Loss on Ignition of Great Bay Sediments

Loss on ignition (LOI) testing was performed on sediments to estimate the amount of organics present. It is important to determine the organic content in the sediments as it may impact the strength (Kosmatka et al. 1991), and possibly have influence on the carbonation of the sediments. The organic content of the Great Bay sediments was 4.2% ± 0.05%. Organic content was measured by heating the sample to 550°C.

The carbon content of Great Bay sediments was also determined by loss on ignition method. The sediments were heated to 950°C and the weight loss between 550°C – 950°C, was the amount of CO₂ evolved from carbonate minerals. It was critical to determine initial carbon content of sediments to ensure
the effect of carbonation on the sediments. The carbon content of uncarbonated
Great Bay sediments was 1.69% ± 0.03% and carbon content of carbonated
Great Bay sediments was 1.72% ± 0.04%. The results showed no significant
difference in the amount of carbon content in the carbonated and uncarbonated
Great Bay sediments. This showed that the raw sediments contained very less
quantity of calcium oxide phases; hence after carbonation there was no formation
of additional carbonate minerals. This illustrated the effect of carbonation
treatment on raw sediments.

4.2 Mixture Design Characterization and Optimization of Process

The mixture design characterization results are divided into five
subsections. The first section includes the results of water content in the mixture.
The second section discusses the different type of binders considered. The effect
of binder content in the mixture design is covered in the section three. Section
4.2.4 contains the results from various methods used for carbonation. This
section explains the methods based on mechanism (instrument) and based on
time. Also presented with the methods is time of carbonation results. Finally,
comparison between the methods on the basis of results obtained from loss on
ignition and thermo gravimetric analysis are presented in section 4.2.5.

4.2.1 Water Content

Water content is an important factor in process of carbonation. As
discussed in Chapter 2, water content affects the CO₂ uptake. Too much water
blocks the pores between the solid particles, restricting the penetration of CO₂
throughout the sample hence, results a decrease in carbonation. Also, too much water can delay the reaction (Johnson 2000, Lange et al. 1996c). Water is the medium for reaction to take place hence; too little water is insufficient for the complete carbonation (Johnson 2000; Klemm and Berger 1972). Hence, there is a need of an optimum water content. The water content varies with the type of material and type of binder.

![Figure 4.2-1: Effect of water content on CO₂ uptake at constant binder content. Optimum water content is approximately 20%.](image)

Five samples of the material were investigated. Water content was varied between 10% and 30%. All the five samples were replicated. The binder content was limited to 10% by total mass. Portland cement was used as a binder. Small changes in water content affected the carbonation significantly. As seen in the
Figure 4.2-1, the optimum water content for Great Bay sediments with portland cement as a binder was approximately 20%. Figure 4.2-1 illustrates that at more than the optimum water content, the addition of water resulted in the reduction of CO₂ uptake. It is important to take into account that optimum water content value may not be same for other types of material. Optimum water content is based on kinetics of reaction i.e. the speed with which a carbonation reaction occurs and the factors that affect this speed. The optimum water content is the amount of water just enough to coat all the particles in thin film, allowing the complete reaction to take place. The factors those affect the speed of reaction is water content and diffusion of CO₂. As there is 100% CO₂ atmosphere, there is enough CO₂ that could be diffused in the thin water film surrounding material particles. However, if the pores are saturated, the diffusion of CO₂ is not throughout the pore space. The diffusion is a much slow process than the CO₂ moving to the water film in a gas form. Too much water i.e. water content greater than optimum water content saturate the pore spaces and the process becomes more dependent on diffusion to move the CO₂. This slows the whole process down. Eventually, all the carbonation may take place, however this could take lot of time. Considering the practical amount of time, optimum water content is considered to be the water content that creates the most calcium carbonate.

4.2.2 Type of Binder

As discussed in Chapter 2; the binder composition affects the carbonation reaction. The Ca(OH)₂, CaO or MgO phases react with carbon dioxide to form CaCO₃ (Klemm and Berger 1972). Three types of binders were used in the
preliminary studies, type II portland cement, cement kiln dust (CKD) and class-F coal fly ash (CFA-F). Carbon dioxide reacts with calcium phases in presence of water to form calcium carbonate in the process of carbonation. In this research, portland cement was used as a binder, as it was readily available, it has been previously used successfully in the S/S treatment of waste in many studies, reducing the metal mobility. It was assumed that if the effectiveness of accelerated carbonation technique is proved by using cement, other types of binders could be considered for future work.

4.2.3 Binder Content

The four samples were investigated at different portland cement (PC) contents while water content was kept constant. The water content was restricted to 10% by total mass. Portland cement content was varied from 10% to 30%. Figure 4.2-2 shows variation in the carbonation i.e. CO₂ (%) uptake with respect to PC content. CO₂ uptake increased with an increase in PC content. The CO₂ (%) uptake at 17% and 25% showed a difference of more than 1%. There was no significant change in the results from 25% and 30% binder content. Hence, the optimum binder content for Great Bay sediments was 25%. It may appear that, as the binder content increases the carbonation would increase, however proximity of individual binder particles would increase resulting in layering of binder. This may cause the saturation of binder in the outer layer acting like a barrier for the diffusion of CO₂ and limiting the extent of reaction (Barnard et al.2004).
Figure 4.2-2: Effect of portland cement content on CO$_2$ uptake at constant water content 10%. The optimum portland cement content is around 25% by mass.

The CO$_2$ uptake is theoretically possible to combine with portland cement during carbonation, is given by Equation 4.1 (Steinour 1959)

$$\text{CO}_2(\text{Theory}) = (0.785(\text{CaO} - 0.6\text{SO}_3)) + (1.091\text{MgO}) + (1.420\text{Na}_2\text{O}) + (0.935\text{K}_2\text{O})$$

[Equation 4.1]

Theoretical CO$_2$ uptake for mixture containing 65% sediments, 25% portland cement and 10% water was calculated using Equation 4.1. William Nourse performed oxide analysis on Great Bay sediments and portland cement (Nourse 2005). For Great Bay sediments, weight of oxides was taken from Table 3.1-2 and for portland cement it was taken from Table 3.1-2. The comparison of actual CO$_2$ uptake and theoretical CO$_2$ uptake is shown in the Figure 4.2-3. It can
be seen that there was a lot more carbonate-able material as percentage of binder increased. The actual results would be greatly affected by mixing and carbonation process. Diffusion of CO$_2$ in the aggregates is discussed in detail later in this Chapter. Theoretical CO$_2$ uptake was 18.99%. Theoretical CO$_2$ uptake was significantly more than actual CO$_2$ uptake 5.2% at 25% cement content. This could be because of precipitation of CaCO$_3$ in the outer portion of the aggregate. As mentioned earlier, after 25% of portland cement addition, any further addition of cement did not increased CO$_2$ uptake.

![Graph](image)

**Figure 4.2-3**: Comparison between actual CO$_2$ uptake and theoretical CO$_2$ uptake with varying percentage of portland cement at constant water content 10%.
4.2.4 Methods of Carbonation

This section is divided into two subsections. The first subsection deals with the results of carbonation process with respect to procedure. The second subsection covers the results from methods of carbonation with respect to time.

4.2.4.1 Method of carbonation with respect to procedure -

Three different types of methods (mixer, column and tumbler) were used to carbonate the samples. As discussed in Chapter 3, the mixer method failed in mixing and carbonating the sample uniformly. At first water was added slowly to the dry sediments. Once the water and sediments were thoroughly mixed, a known quantity of the portland cement was added to the mixture. In this process, portland cement was not uniformly distributed all over the mixture because lumps of sediments were formed immediately after addition of water. Subsequently, sediments and portland cement were dry mixed in the stand mixer and then the water was added gradually. Also, it was observed that the sample was too wet after introduction of carbon dioxide in the container of the stand mixer. This extra water in the sample was released during the carbonation process. Also, the aggregates were very small, and didn't simulate field conditions. Hence, it was decided to use the stand mixer only for the mixing of dry material with water. Later, the mixture was carbonated in either column or in a tumbler. Detailed methods of carbonation in the column and in a tumbler were explained in Chapter 3. The latter two methods were compared by plotting TGA results shown in Figure 4.2-4. The mixture with 16.5% portland cement, 16.5% water and 67% sediments was carbonated in a column and in the tumbler. The results from TGA
revealed that more CO$_2$ was evolved between 600°C and 800°C for column carbonation. However, considering derivative scale i.e. rate of change of weight with respect to temperature showed negligible difference in the methods. With the percent weight change the column carbonated samples evolved approximately 1% more carbon dioxide than that of the tumbler carbonated samples. The weight change difference was so negligible that it was ignored.

![Figure 4.2-4: TGA graph showing comparison between column and tumbler carbonation method.](image)

**Figure 4.2-4**: TGA graph showing comparison between column and tumbler carbonation method.

**4.2.4.2 Methods of carbonation with respect to time -**

Two different methods of carbonation were adopted (a) Continuous carbonation and (b) Cyclic carbonation. A mixture of 16.5% portland cement, 16.5% water and 67% sediments was carbonated. The detailed procedure for continuous carbonation and cyclic carbonation was explained in section 3.2.
Figure 4.2-5 shows the TGA graph of comparison between both the processes. The derivative curve (dotted line) showed spike between temperatures 600° C and 800° C, which was the amount of CO$_2$ evolved during heating. The results for both the methods were compared in this particular temperature range. Cyclic carbonation appeared more significant than continuous carbonation. The comparison between the peaks showed the difference of 2.5% weight change which was significant considering the total CO$_2$ uptake.

The better performance of cyclic carbonation may be justified as better diffusion of carbon dioxide or better degree of carbonation. In cyclic carbonation material was crushed after an interval of 1 hour and loss of water due to heat of evolution was made up. The better performance due to crushing may be explained as, sediments contained significant amount of clay, during initial mixing and carbonation clay lumps may have formed. Clay lumps reduced the diffusion of carbon dioxide in the material. With the crushing these lumps were disintegrated making the material more adaptive for further carbonation.
4.2.4.3 Time of carbonation -

A sample with 20% water content, 25% portland cement and 55% sediment content was carbonated for five hours. The samples collected after every one hour interval were tested for CO₂ uptake. There is an increase in carbonation with the increase in time of process (Bukowski and Berger 1979). However, after a particular time, the rate of reaction decreased with the further carbonation as seen in Figure 4.2-6. It can be observed that during the first 1 hour, the carbonation reaction was rapid and that with the further carbonation the rate of carbonation was reduced. After 2 hours of carbonation, the rate of carbonation was decreased significantly. The CO₂ uptake (%) observed after 2 hours of carbonation was considerably equal to the CO₂ uptake (%) after 5 hours.
of carbonation. It was clear from Figure 4.2-6, the CO₂ uptake observed was not directly proportional to the time of carbonation. The reduction in the rate of carbonation between 2 and 5 hours compared to initial 2 hours of carbonation could be due to saturation of reaction product filling the pore space and thereby decreasing the further CO₂ uptake in the material.

![Graph showing CO₂ uptake with respect to time](image)

**Figure 4.2-6: CO₂ uptake with respect to time**

### 4.3 Statistical Modeling and Discussion

Once the experimental design was established, the data was collected for statistical analysis using JMP®. The details of design of experiments using mixture design were discussed in Chapter 3. The desired response was maximum percentage of CaCO₃ obtained after the accelerated carbonation treatment. This section discusses the statistical modeling and the optimum mix proportion of the components. The data was analyzed in the fit model platform.
Often times important conclusions about a model can be drawn from graphical analysis techniques (Snee 1985). Graphical analysis is covered later in this section.

4.3.1 Modeling Results and Discussion

Mixture experimental results are modeled using regression analysis. Equation 4.2 represents general mixture regression model.

\[ Y_{ij} = \sum_{i=1}^{q} \beta_i X_i + \sum_{1 \leq i < j \leq q} \beta_{ij} X_i X_j \]  \hspace{1cm} \text{[Equation 4.2]}

Where:
- \( \beta \) = coefficient constant for model term
- \( X_i \) = factor setting for the \( i^{th} \) factor
- \( X_j \) = factor setting for the \( j^{th} \) factor
- \( Y_{ij} \) = predicted response

The general mixture model shown in Equation 4.2 is similar to linear regression model except the intercept term \( \beta_0 \) is removed. Intercept represents the value when all the components are set to 0 and in the mixture design components cannot be simultaneously set to 0 proportion. For the technical reasons an R-squared term was not provided with the no intercept option in the Fit model.

It is possible to refine the model to an optimal form by using the process of screening. This can be achieved by removing non-significant terms from the full model to create final significant model. The first screening step is removing the non-significant interaction terms. The interactions having highest prob>|t|, greater
than accepted probability 0.05 are removed one at a time. After every removal
done one at a time, model must be recomputed to determine new significant and
non-significant terms. This is continued till all the terms are significant in the
whole model. However, it is important to note that the test of significance for pure
blends (pure components like portland cement, sediments or water) are ignored
since pure components cannot be removed from the mixture.

As it can be seen in Table 4.3-1, the full model consists of all pure blends
(pure components) and binary blends (interacting components). As per the above
stated process of refining, interaction ‘sediments\star portland cement’ had the
highest prob>|t| (known as p-value) of 0.4989 which is greater than accepted
probability 0.05. Hence it was removed from the model and the model was
recomputed. The new model shown in Table 4.3-1, as Final Model was obtained.
There are no more non-significant interactions in this model. The test of
significance for portland cement was ignored although it had p-value of 0.1434
which is greater than 0.05. It is not possible to remove the portland cement from
the mixture.
<table>
<thead>
<tr>
<th>Terms</th>
<th>Full Model</th>
<th></th>
<th></th>
<th>Final Model</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Mixture</td>
<td>Coefficient Estimate</td>
<td>Standard Error</td>
<td>t-Ratio</td>
<td>Prob&gt;</td>
<td>t</td>
<td></td>
</tr>
<tr>
<td>Intercept</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>Water</td>
<td></td>
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<td>-4.03</td>
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</tr>
<tr>
<td>Portland Cement</td>
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<td>28.454</td>
<td>1.04</td>
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<td>10.164</td>
<td>6.527</td>
</tr>
<tr>
<td>Sediments</td>
<td></td>
<td>-3.257</td>
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<td>-1.29</td>
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<tr>
<td>Water*Portland Cement</td>
<td></td>
<td>136.056</td>
<td>51.539</td>
<td>2.64</td>
<td>0.0216</td>
<td>157.818</td>
<td>40.199</td>
</tr>
<tr>
<td>Water*Sediments</td>
<td></td>
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<td>3.73</td>
<td>0.0029</td>
<td>135.489</td>
<td>34.897</td>
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<tr>
<td>Sediments*Portland Cement</td>
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<td>-29.690</td>
<td>42.574</td>
<td>-0.7</td>
<td>0.4989</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The final mixture model is given by Equation 4.3 which would predict the outcome for the studied process. The model accommodated pure components as well as interaction between components.

\[
\% \text{ CaCO}_3 = 10.164(\text{portland cement_ } \%) - 4.335(\text{sediments_ } \%) - 87.341(\text{water_ } \%) + 157.818(\text{water_ } \% \times \text{portland cement_ } \%) + 135.489(\text{water_ } \% \times \text{sediments_ } \%)
\]  

[Equation 4.3]

4.3.2 Optimization and Discussion

After the modeling results were obtained, graphical analyses techniques were used to verify the overall significance of the model. The actual by predicted plot is very important tool in statistics which depicts the overall performance of a statistical model. If all the data points would fall on a 45-degree line, it is concluded that the model fits the data perfectly. Points falling above 45-degree line indicate model is under predicting and points falling below indicate model is over predicting. The curved lines represent confidence intervals. Using 95% confidence and response mean, significance of the model can be determined. Figure 4.3-1 shows the actual by predicted plot. Theoretically, if the response mean line is surrounded by confidence curves the model is insignificant i.e. model may be no different than the mean. If the response mean line and confidence curves intersect each other at some angle, the model is considered to be significant. As seen in the Figure 4.3-1, most of the points fall within confidence interval curves. Also, actual by predicted plot shows that confidence
interval curves cut response mean line at sharp angle. This shows model is highly significant. Another test to evaluate significance of the model is to check probability i.e. p-value of the model. The prob>F (p<0.0001) of the model is less than 0.05 which indicates model is significant.

![Actual by Predicted Plot](image)

**Figure 4.3-1 : Actual by predicted plot of %CaCO₃ data**

Prediction profiler is the tool used to predict the optimize response from the experiments. It is a graphical display of the statistical model linking water, portland cement and sediments with CaCO₃. It allows changing the settings of one factor and corresponding change in response of other factors. Figure 4.3-2 shows prediction profiler along with desirability.
With the help of desirability function, the response was maximized and optimum settings of all the three factors were determined. Desirability ranges from 0 to 1, where 0 represents lack of fit and 1 represents perfectly fit model. The prediction profiler in Figure 4.3-2 shows the optimum settings for the factors. As can be seen all the factors have a significant impact on the CaCO₃ content. If the desirability trace is curved, it indicates the process needs to be closely controlled because any changes in the factor setting have a significant effect on the desired response. Hence, the water content need to be fine tuned and is set on 20% for maximum desirability. Table 4.3-2 shows the mixture design needed for the maximum response i.e. it is the optimum mix proportion obtained from statistical analysis. The ternary plot in Figure 4.3-3 shows the position of the optimum mix proportion in the mixture space.
Table 4.3-2: Optimized mixture design (percent by mass)

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment (%)</td>
<td>55.34</td>
</tr>
<tr>
<td>Portland cement (%)</td>
<td>25</td>
</tr>
<tr>
<td>Water (%)</td>
<td>19.66</td>
</tr>
</tbody>
</table>

Figure 4.3-3: Ternary plot showing optimum mixture

Interaction profiles are graphical methods used to predict the interaction among the factors. Figure 4.3-4 shows the interaction between water, portland cement, and sediments. When two or more of the factors in the experiment show significant interaction, the lines representing those factors appear to intersect each other, however, if there is no interaction between the factors, the lines are parallel to each other.
According to the interaction plot shown in Figure 4.3-4, the parallel lines in the interaction plot confirm that portland cement and sediments do not appear to have a significant interaction. The impact of portland cement on %CaCO$_3$ is independent of the setting of sediments and vice versa. On the other hand, significant interaction was seen between water and portland cement, and water and sediments. In this case, both the interactions were significant when water content was set on optimum level of 20% (See Figure 4.3-4). The nature of interactions supports the theory behind experiments. In the process of
carbonation of material water act as a medium of change i.e. without water there is no significant reaction between portland cement and sediments. The impact of water on the formation of CaCO₃ is highly significant.

The results of physical characterization as well as environmental assessment of the artificial aggregates produced in the mini concrete mixer are discussed next this chapter.

**4.4 Detailed Characterization of Artificial Aggregates**

This section describes the detailed characteristics for the optimized mixture which was comprised of 55% sediments, 25% cement and 20% water. The artificial aggregates were made in mini concrete mixer using the method of carbonation discussed in section 3.3. In this section results are presented from the findings of water content, sieve analysis, modified proctor test and CBR. This section also presents the results from scanning electron microscopy and thermogravimetric analysis.

**4.4.1 Scanning Electron Microscopy**

The aggregate sample of optimized mixture was examined using scanning electron microscopy. This allowed a more detailed study of the carbonation product development in the artificial aggregate. Schematic of different layer formation is shown in Figure 4.4-1. An aggregate with 2.5 cm diameter was broken into half to examine the depth of carbonation.

It was observed that there were two distinct zones of carbonation (Figure 4.4-2). The extent of carbonation was not uniform throughout the aggregate.
Hence, it was decided to divide the aggregate in three zones: cover, transition/intermediate and center. The images of each zone were taken using scanning electron microscopy.

![Figure 4.4-1: Schematic of CO₂ in artificial aggregate](image)

It was seen from the scanning microscopy images that the carbonation i.e. formation of CaCO₃ changes with respect to depth. The images were captured at different points varying from cover of aggregate to the centre/core of an aggregate. Thin section analysis, Figure 4.4-3 through Figure 4.4-5 showed calcium carbonate, which was a product of the reaction between cement and water after carbonation, was observed to develop. The needle like crystals of CaCO₃ was easily seen in Figure 4.4-3 in the cover zone of aggregate. As we moved from cover to the intermediate zone of an aggregate the amount of CaCO₃ crystals was reduced as shown in Figure 4.4-4. Finally, the image taken at the centre of aggregate showed negligible amount of crystals of CaCO₃, can be seen in Figure 4.4-5. Other unidentifiable particles exist in Figure 4.4-6 were
most likely clay minerals, organic matter and other foreign materials from the dredged sediments.

The findings from scanning electron microscopy confirmed that the degree of carbonation varies with the depth which is shown in Figure 4.4-2. Further, to ensure these results, TGA was performed.

Figure 4.4-2: Layers in artificial aggregate. The first image shows the half cut aggregate with layers of different shades of grey. The second is SEM image with the magnitude of 1 mm.
Figure 4.4-3: SEM photomicrograph showing a needle shaped calcium carbonate crystals. Image is of cover zone of an aggregate.

Figure 4.4-4: SEM photomicrograph showing a needle shaped calcium carbonate crystals. Image is of intermediate zone of an aggregate.
Figure 4.4-5: SEM photomicrograph showing a needle shaped calcium carbonate crystals. Image is of core of an aggregate.

Figure 4.4-6: SEM photomicrograph showing organic matter and possibly clay minerals.
4.4.2 Degree of Carbonation using Thermo Gravimetric Analysis (TGA)

Examination of half cut aggregate from scanning electron microscopy revealed that the carbonation was not uniform throughout the aggregate. The degree of carbonation changed with respect to depth. There was another factor which affected the degree of carbonation. It was observed in the grain size analysis, the aggregates were uniformly graded. As seen in Figure 4.4-7, the size of aggregate varied from 1 cm to 5 cm. The other factor which affected the degree of carbonation was size of an aggregate.

Thermogravimetric analysis was performed to determine the variation of carbonation with respect to size of an aggregate. Samples were randomly selected, varying in diameter from 1 cm to 4 cm. Each aggregate was cut into half. A small sample was taken from cover and also from center of an aggregate. Figure 4.4-7 presents a bar chart that graphically represents the results of degree of carbonation for each zone.

As was expected from the SEM results, the carbonation was more effective in outer region than central region. Also, the size of aggregate had an effect on degree of carbonation. As it is seen in Figure 4.4-7, in the small aggregate (say 1 cm) the difference in percentage of calcium carbonate in core and in cover was less. However, as the size of aggregate increased the difference in calcium carbonate from cover to core also increased. This may be caused by precipitation of CaCO₃ in the outer part of an aggregate, restricting the sequestration of CO₂ inside aggregate.
4.4.3 Water Content of Artificial Aggregates

During the process of formation of artificial aggregates it was observed that some material was accumulated at the bottom of the drum. This bottom material was lumped and was wetter and stickier than artificial aggregates (Figure 4.4-8). The water content of artificial aggregates immediately after mixing was averaged 23.58% and the water content of bottom material was averaged 24.99%. The results from water content testing of both the materials showed that bottom material contained more clay, which holds the water during the process of carbonation. To minimize the quantity of bottom material, intermediate stirring is important. The original amount of water added to the material was 20% by total mass of material however; there was an increase of approximately 3.58% of water content in the final product. It was clear from the results that the additional
water in the artificial aggregates was the result of exothermic carbonation process in which extra water was liberated during the process.

Figure 4.4-8 : Water content of bottom material and artificial aggregates

4.4.4 Particle Size Distribution

The particle size distribution of artificial aggregates was performed according to AASHTO T 27-99. The particle size distribution curve, presented in Figure 4.4-9, shows that more than 90% of artificial aggregates consist of aggregates with diameter less than 37.5 mm (1-1/2"). The particle size distribution was performed before crushing the artificial aggregates. The particle size distribution curve demonstrated uniform gradation of artificial aggregates. Uniform gradation refers to a gradation that contains most of the particles in a very narrow size range. Figure 4.4-10 shows different size aggregates in the 2'x2' metal tray.
4.4.5 Modified Proctor Test

Compaction tests were performed according to modified Proctor method, AASHTO T 180-01. In Figure 4.4-11, the compaction curve was plotted for a
water content ranging between 10% and 26%. For artificial aggregates, the maximum dry unit weight and the optimum water content are equal to 1.53 gm/cm³ and 24.35% respectively. The optimum water content is the water content that results in the greatest density for a specified compaction effort. It was also observed that aggregates were broken up during the testing.

![Modified Proctor Test Curve](image)

**Figure 4.4-11: Compaction curve for artificial aggregates**

### 4.4.6 California Bearing Ratio (CBR)

The California Bearing Ratio (CBR) was used to measure the bearing capacity of a compacted material. The likely disintegration of artificial aggregates posed the question whether to treat the material as aggregates or soil. The realistic approach was to perform CBR on the material. For heavy compaction,
material was compacted in 5 layers, 56 blows to each layer. The optimum water content of 24.35% was used which was obtained in modified proctor test. The detail procedure was explained in Chapter 3.

![Graph showing CBR value](image)

**Figure 4.4-12: CBR value**

Figure 4.4-12 shows the plots between 0 and 0.2 inches of penetration (except for the 0.3 inch penetration test). The test is normally done until about 0.300 inches of penetration in the soil, however, because of some technical difficulty observations were taken with penetration till 0.2 inches.

The corrected zero deflection mark was applied by extending the linear portion of the plot down to the x-axis. Corrected loads for 0.1 inch penetration and 0.2 inch penetration were used to calculate CBR values. The CBR values were calculated using Equation 3.3. The standard load for 0.1 inch penetration
was 1000 psi and for 0.2 inch penetration was 1500 psi. Table 4.4-1 shows CBR values for 0.1 inch and 0.2 inch penetrations.

<table>
<thead>
<tr>
<th>Penetration (in)</th>
<th>CBR Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>31.3</td>
</tr>
<tr>
<td>0.2</td>
<td>40.4</td>
</tr>
</tbody>
</table>

Normally, the CBR number is taken to be that achieved by the 0.1 penetration, since that is predominantly the larger value. If the CBR given by the 0.2 inch penetration is larger, then the test is to be redone. If on the second attempt the penetration is larger for 0.2 than 0.1 once again, use the load for 0.2 inch penetration. In this case, for each test the CBR value was larger for 0.2 inch penetration, therefore the CBR value for this material was 40.4%. According to the Unified Soil Classification System, CBR range for GW type is 40-80. GW type is well graded gravels and gravel sand mixtures. For artificial aggregates, CBR value (40.4 %) was within the range of GW type material.

4.5 pH Dependent Leaching of Artificial Aggregates

The pH dependent leaching test is used to evaluate how differences in the environmental pH affect the leaching behavior of materials as well as for an assessment of the acid buffering capacity of the material (van der Sloot et al. 2001). The pH dependent leaching test can be used to characterize leaching
properties of metals in various management environments including areas of low pH such as municipal solid waste landfills and areas of high pH such as sediments solidified and stabilized with cement (Tsiatsios 2005). The solubility of many metals depend on pH, hence if the pH of the material is likely to change in any management environment, then it is important to determine its leaching behavior at the range of expected pH values.

The ageing processes of the materials such as aging of MSWI bottom ash may cause changes in the speciation of contaminants and decrease in the pH, mainly because of CO$_2$ uptake (Brouwer et al. 2006). The pH dependent leaching tests were performed using a LS ratio (liquid to solid ratio) of 10 and by using HNO$_3$ and NaOH as extracting solution. The detailed test specifications were discussed in Chapter 3. The pH of a material treated using S/S with an alkaline binder such as cement or lime is generally between 11 and 13 (Cocke and Mollah 1993). In the carbonation reaction, carbonic acid (H$_2$CO$_3$) formation lowers the pH of the material. Cecile Pouly observed that the pH of Newton Creek (NC) sediments was 6.4 initially. pH of NC sediments solidified/stabilized with cement and CFA was 11.05 whereas the same material after accelerated carbonation had a pH of 9.24 (Pouly 2005). The natural pH of Gowanus Canal sediments was 6.7. The pH of carbonated artificial aggregates (55% Gowanus Canal sediments, 25% portland cement, 20% water) was 8.1. Christopher Tsiatsios stabilized Gowanus Canal sediments with 7% cement. He observed that the natural pH of the sediments increased from approximately 7.5 – 8.7 to 11.2 – 12.2 after stabilization. The reduction in the pH of artificial aggregates
treated with 25% cement was because of the carbonation process. The results of pH values of sediments treated with different methods are summarized in the Table 4.5-1

<table>
<thead>
<tr>
<th>Natural pH of Untreated Sediments</th>
<th>pH of Artificial Aggregates (Accelerated Carbonation)</th>
<th>pH of S/S Treated Sediments</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7</td>
<td>8.1</td>
<td>11.2-12.2</td>
</tr>
</tbody>
</table>

The leaching behaviour of artificial aggregates as a function of pH was evaluated and compared with the leaching behaviour of the raw Gowanus Canal sediments. The results of pH dependent leaching tests are given in Figure 4.5-1 – Figure 4.5-6. In general, an amphoteric behaviour was observed for Cd, Cr, Cu, Ni, Pb and Zn. As seen in the figures, leachability of the material was higher at low and high pH values than at neutral pH values.

Two types of trends were observed in the leaching behavior of untreated sediments and artificial aggregates. The first trend showed an overall similarity between the leaching behavior of untreated and treated sediments, except the treated sediments released less metals. For example, for Cr (Figure 4.5-2) and Cu (Figure 4.5-3) treated GC sediments followed the similar trend as untreated sediments between a pH range of 4 - 12 with the exception of reduction in the element concentration in treated sediments. The second trend showed similar element concentrations for the acidic pH range (pH < 7) and significant reduction in element concentration for basic pH values (pH >8). For example, for Cd
(Figure 4.5-1), Ni (Figure 4.5-4), Pb (Figure 4.5-5) and Zn (Figure 4.5-6), at low pH values (pH < 7), there was no significant change in the release of metals from untreated GC sediments and carbonated artificial aggregates, whereas at high pH values (pH > 8), the released metal concentration decreased in artificial aggregates. The reduction in the release of metals at high pH values demonstrated stable behavior of carbonates whereas at lower pH values there might be a change in the controlling mechanism of contaminants. It is important to note that the metals were diluted by addition of portland cement in artificial aggregates compared to the raw sediments. However, the results presented in the graphs show direct comparison between untreated raw sediments and artificial aggregates as after application of artificial aggregates in the field, the regulators are going to evaluate the leaching of actual treated artificial aggregates.

Maximum contaminant levels (MCLs), calculated using LS ratio of 10ml/g, were used as a reference points. MCL is the highest level of a contaminant that is allowed in drinking water (USEPA 2009). At extreme pH values (pH < 6 and pH >10) most of the metal concentrations were above MCLs. This indicated that metals were more susceptible for leaching at extreme pH environment. Figure 4.5-7 shows, comparison of element concentration for MCL, untreated sediments and artificial aggregates (treated sediment). Also, comparison between solidification/stabilization (S/S) technique and accelerated carbonation technique on the basis of pH dependent leaching of Gowanus Canal sediments is shown in Figure 4.5-7. The element concentration was measured at natural pH value.
Natural pH of untreated Gowanus Canal sediments, carbonated sediments and SS sediments was 6.7, 8.1 and 11.7 respectively. The results for S/S Gowanus Canal sediments were adopted from Christopher Tsiatsios (Tsiatsios 2005). In general, Gowanus Canal sediments treated with accelerated carbonation technique demonstrated less leaching potential than solidified/stabilized sediments at natural pH value. Cr showed similar results for both the treatment techniques. It is important to note that SS treatment was performed using 7% cement and accelerated carbonation was performed using 25% cement as a binder. Also, LS ratio for S/S sediments was 12.1 mL/g, whereas for carbonated sediments was 10 mL/g. The difference in the leached metal concentration was mainly due to reduction in the pH of carbonated sediments than SS sediments.

The overall results obtained for carbonated sediments revealed that Cd, Cr, Cu, Ni, Pb and Zn were effectively stabilized and were below the MCL. Although, the leached metal concentration of artificial aggregates for Lead is close to MCL, it is important to note that the aggregates were crushed for running the tests whereas during actual application scenario the crushing of aggregates is not likely. This is true for all the other elements so as to ensure better performance of the artificial aggregates in the field.
Figure 4.5-1: pH-dependent leaching of Cadmium from treated and untreated Gowanus Canal sediments

Figure 4.5-2: pH-dependent leaching of Chromium from treated and untreated Gowanus Canal sediments
Figure 4.5-3: pH-dependent leaching of Copper from treated and untreated Gowanus Canal sediments

Figure 4.5-4: pH-dependent leaching of Nickel from treated and untreated Gowanus Canal sediments
Figure 4.5-5: pH-dependent leaching of Lead from treated and untreated Gowanus Canal sediments

Figure 4.5-6: pH-dependent leaching of Zinc from treated and untreated Gowanus Canal sediments
Figure 4.5-7: Comparison of element concentration for MCL, untreated sediments, artificial aggregates and stabilized sediments at their natural pH value

(Leaching data for SS Gowanus Canal sediments was adopted from Christopher Tsiatsios, 2005)
CHAPTER 5

CONCLUSIONS

The purpose of this research was to show that dredged sediments could be utilized as artificial aggregates by enhancing the sediment properties. The ultimate goal was to develop an alternative technique for the safe use of mildly contaminated sediments. In addition, the development of statistical model was an important feature to predict the performance of the material.

This research was successful in the production of artificial aggregates showing the beneficial use of dredged contaminated sediments. The enhanced physical properties along with improved leaching behavior will enable mildly contaminated dredged sediments to be considered as a resource rather than a waste.

This chapter is divided into four sections. The first section discusses the conclusions derived from this research. The second section is about recommendations and considerations for future research on artificial aggregates. The scope of future work related to this research topic is presented in the third section. Finally, remarks on the overall project are covered in the last section.
5.1 Conclusions

The following conclusions are derived for Great Bay sediments and Gowanus Canal sediments. The results may vary depending on the basic properties of the dredged sediments.

1. The results of water content experiments showed that the water content had a great effect on the CO₂ uptake of the material. At 20% water content the CO₂ uptake was optimum with portland cement used as a binder. The optimum water content is important as insufficient water causes an incomplete carbonation reaction, while too much water halts the reaction by slowing diffusion.

2. There was a significant effect of cement content on CO₂ uptake. The CO₂ uptake increased with an increase in cement content. At 25% portland cement content, optimum carbonation was achieved. Beyond 25% binder content the mechanism affected the reaction reducing the efficiency of CO₂ uptake. It was thought that in small grained material at the higher binder content the pores get clogged reducing the efficiency of carbon dioxide diffusion in the material.

3. The time of carbonation was limited to 2 hours as further carbonation had significantly low effect on CO₂ uptake. It was concluded that with sufficient diffusion of carbon dioxide calcium carbonate precipitated causing difficulty in further diffusion of CO₂ and formation of CaCO₃.

4. Through testing of different mechanisms for carbonation, cyclic carbonation was more efficient than continuous carbonation, as in cyclic
carbonation each time material was crushed increasing the capacity of CO₂ uptake.

5. Material mixing procedure was influenced by sequence of material addition and method of carbonation. Addition of water to sediments initially and then addition of cement resulted in formation of lumps of sediments and uneven carbonation. Dry mixing of material and later addition of water was found to be most appropriate method. This is an important conclusion as natural water content of dredged sediments is very high hence the binder mixing procedure is going to be challenging.

6. The use of different methods in the process of carbonation suggested that, there was no significant difference in CO₂ uptake when carbonation took place in tumbler or in column.

7. The design of experiments was successful using the following factor range in terms of percent mass: 40 to 82% of sediments, 7.8 to 30% of portland cement and 9.2 to 30% of water.

8. JMP® Statistical analysis using Fit Model theory for mixture design predicted the optimum mix proportion of 55% sediments, 25% portland cement and 20% water. Portland cement content will likely be determined by cost vs. performance. The results were compared and confirmed using prediction profiler with actual mixture performance on the basis of formation of calcium carbonate. Statistical analysis was performed only for samples made with Great Bay sediments.
9. Petrography showed the development of needle shaped calcium carbonate crystals. Diffusion of CO\(_2\) was not uniform from the cover to the center of an aggregate. Petrography analysis showed more CaCO\(_3\) crystals in outer area and less CaCO\(_3\) crystals in central area of an aggregate. Organics were observed in artificial aggregates which could cause decay over time. The results from scanning electron microscopy were supported by thermogravimetric analysis of an aggregate. The diffusion of CO\(_2\) from the cover to the center varies with size of an aggregate. It was found that in smaller size aggregates carbonation was uniform however, as size increased carbonation was more in outer area of an aggregate while inner part remained uncarbonated. This result was important as over the time aggregate would most likely disintegrate or crushing of an aggregate might expose the inner uncarbonated material.

10. Artificial aggregates comprise of optimum mix proportion and made in mini concrete mixer were characterized using AASHTO methods for sieve analysis (particle size distribution), Modified Proctor test and CBR. The results of particle size distribution showed uniformly graded aggregates. The Modified Proctor test enabled maximum degree of compaction at the water content of 24.53% with maximum dry density of 1.53 gm/cm\(^3\). The results of Modified Proctor test were obtained in accordance with AASHTO T180-01. CBR values for 0.1 inch deflection are 46.5 % and for 0.2 inch penetration is 61 %. In this case CBR value for 0.2 inch deflection was considered as in both the attempts the load values were higher for
deflection 0.2 inch than deflection 0.1 inch which were specified in AASHTO T193-99.

11. The pH dependent leaching test was performed with LS ratio of 10 to determine the effect of accelerated carbonation on metal immobilization in aggregates made up of contaminated sediments. Gowanus Canal sediments were used in artificial aggregates. In general, the release of metals decreased in carbonated sediments compared to uncarbonated sediment. The pH of raw Gowanus Canal sediments, solidified/stabilized sediments and carbonated sediments was 6.7, 11.7 and 8.1 respectively. Reduction in the pH value was observed from hydrated sediments to carbonated sediments. Metal concentrations of carbonated sediments were below MCL specified by US EPA. Accelerated carbonation worked better for metals such as Cd, Cr, Cu, Ni, Pb and Zn at natural pH values. Comparison between traditional S/S treatment and accelerated carbonation technique revealed accelerated carbonation technique is more effective in metal retention.

5.2 Suggestions and Considerations for Future Research

This research demonstrated the potential for using contaminated sediments (Great Bay sediment and Gowanus canal sediment) as artificial aggregates by the treatment of accelerated carbonation. The following suggestions may improve the further research methods of accelerated carbonation of contaminated sediments.
1. The use of instruments can be limited to obtain preliminary factors in process of carbonation. This will avoid time consumed to decide the most appropriate instrument.

2. Better statistical models could be developed for designing the experiments. The mixture design experiment approach proved effective tool in this research hence, it should be used in this type of research. However, only one response, % CaCO$_3$ was considered. The models could be expanded to consider physical properties. For example, different physical properties such as CBR value, maximum dry density, strength could be considered as a response to develop detailed model.

3. Experiments on material preparation on a larger scale are encouraged as it was difficult to relate small scale experiments with large scale experiments.

4. More emphasis should be given on evaluating physical and chemical properties of the artificial aggregates with spending minimum time on preliminary results like optimum mix proportion, time of carbonation etc.

5. It would be beneficial to construct a setup for mini concrete mixer which has better control over water supply and carbon dioxide supply.

5.3 Future Work

1. Research should be performed on sediments with different physical and chemical properties to determine the influence of sediment type on different parameters in the process of accelerated carbonation. This will
also help in developing general statistical model for treatment on dredged sediments.

2. 25% cement content is very high which makes this treatment expensive. To make the treatment more cost effective, more emphasis should be given to decrease the amount of cement used.

3. Other types of binders, especially calcium silicate based recycled materials should be used. Use of cement kiln dust, different types of fly ashes, blast furnace slag should be examined so that the disposal problem of recycled material is resolved in innovative and beneficial way.

4. Studies should be performed on wet sediments instead of drying and crushing them as it is very tedious and time consuming procedure. Also, this research aims at large scale production of artificial aggregates hence it is not possible to dry and crush all the sediment.

5. In-situ evaluation of the artificial aggregates should be performed to evaluate the impact on physical properties as well as on leaching behavior in the field.

6. Cost estimate for the production of artificial aggregates will help to determine if this research has potential in practical environment.

5.4 Final Remark

Accelerated carbonation of dredged sediments in the form of artificial aggregates can help to solve environmental issues like disposal of mildly contaminated dredged sediments. This treatment method enables to consider
dredged sediments as a resource instead of waste. Other calcium silicate based recycled materials can be used in this research. Accelerated carbonation utilizes carbon dioxide to enhance the properties of the material which causes reduction in green house gas. Considering the rising demand for confined disposal facilities, this treatment improves heavy metal retention in contaminated sediments for their beneficial use application. Artificial aggregates might fulfill the demand of natural aggregates to some extent.
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APPENDIX

Thermogravimetric Analysis Results
Thermogravimetric analysis of pure materials: CaCO3 and Ca(OH)2

**Decomposition of CaCO3 → CaO + CO2**

![Graph showing the decomposition of CaCO3](image)

**Figure 1: Decomposition of CaCO3**
Decomposition of Ca(OH)$_2$ $\rightarrow$ CaO + H$_2$O

Figure 2: Decomposition of Ca(OH)$_2$