Project 34 - Accelerated Carbonation of Contaminated Soils for Beneficial Use Applications

Executive Summary

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INTRODUCTION

The goal of this research was to determine if a new processing technique for contaminated soils and sediment would produce artificial aggregates that could be utilized in beneficial use applications. The artificial aggregates are prepared using an accelerated carbonation technique where soil, water and Portland cement are mixed in a carbon dioxide rich atmosphere to form a solid material that essentially has $CaCO_3$\soil matrix. A statistical design of experiments approach was applied to analyze various artificial aggregate mixtures. In order to determine the key process parameters for process optimization, laboratory scale experiments were performed. 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.

THEORY

For last several years, various types of binders have been used to solidify and stabilize contaminated soils and byproduct materials, with Portland cement being the most common binding agent. In a traditional stabilization/solidification (S/S) process, Portland cement is added to soils to improve the physical and handling characteristics of the material along with limiting the mobility of heavy metals. Accelerated carbonation is an additional step that can be used to enhance the properties of the material.

In the process of accelerated carbonation, carbon dioxide gas (CO_2) is introduced into the mixture of soil and cement in presence of water. The following reaction takes place

- A thin aqueous film is formed around the particles of the soil-cement mixture
- Water reacts with calcium oxide (CaO) phases of the cement to form calcium hydroxide ($Ca(OH)_2$)

$$CaO + H_2O \Rightarrow Ca(OH)_2$$

- Carbon dioxide from surrounding atmosphere gets absorbed into the aqueous film forming carbonic acid (H_2CO_3)

$$CO_2 + H_2O \Rightarrow H_2CO_3$$

- Calcium ions (Ca^{2+}) from the $Ca(OH)_2$ diffuse outwardly to react with CO_3^{2-} forming calcium carbonate ($CaCO_3$)

$$CO_2 + Ca(OH)_2 \Rightarrow CaCO_3 + H_2O$$

The carbonation is exothermic, releasing significant heat as well as free water.

MATERIALS AND METHODS

The basic components used to produce artificial aggregates are soil, Portland cement, water and carbon dioxide. For this research, a silty-clayey sediment was used as the soil on the basis that it represented the most challenging soil type to work with. This research involves optimization of the key parameters along with optimization of mix proportion; therefore a significant number of experiments were conducted. Considering the risks of using different contaminated sediments, disposal and handling of contaminated sediments it was decided to use clean sediments. The clean sediments used were dredged from Adams Point in Great Bay estuary in Maine. For performing the experiments on leaching behavior of contaminated sediments, Gowanas canal sediments were used. Type II Portland cement was used as a binding agent.

Carbonation depends on factors like water content, binder content, time of carbonation method of carbonation etc. Optimization of key parameter was done by performing laboratory scale experiments. In small/laboratory scale experiments sediments and cement were dry mixed in small mixer; water was added gradually into the mixture. Immediately after the uniform mixture was formed samples were carbonated in either columns or tumbler. The efficiency of accelerated carbonation process was evaluated using thermo gravimetric analysis (TGA) for all the samples in terms of CO_2 uptake i.e. formation of $CaCO_3$.

With the help of statistical methods and results from small scale experiments, the optimization of key parameters and process was achieved. A scaled-up version of the optimized process for making artificial aggregates was performed using a concrete mixer (Red lion, model Big cat type B). These artificial aggregates were analyzed using TGA, SEM for carbon dioxide sequestration.

Previous studies have shown that carbonation helps to limit the mobility of contaminants. To verify the performance of contaminated sediments as a form of artificial aggregates against the heavy metal retention is currently in progress using pH dependent leaching test with ICP-AES.

Statistical Methods. Different mix proportions of basic ingredients of artificial aggregates were obtained using mixture design concept from DOE. With the help of statistical software JMP®, optimum experimental points were selected in the mixture space. Based on literature and some preliminary experiments constraints were imposed on each factor. See figure 1 for ternary plot showing the mixture space. After applying the constraints on each factor a narrow experimental region at lower right side was obtained. The focus was to achieve maximum percentage of sediments keeping percentage of PC as low as possible. Applying the constraints, JMP® software chose 24 unique points, each point indicating unique mix proportion.

Component	Constraints	
	Lower Bound	Upper Bound
H_2O	0.091	0.3
Portland Cement	0.078	0.3
Sediments	0.4	0.821

TABLE 1. Constraints on components of artificial aggregates

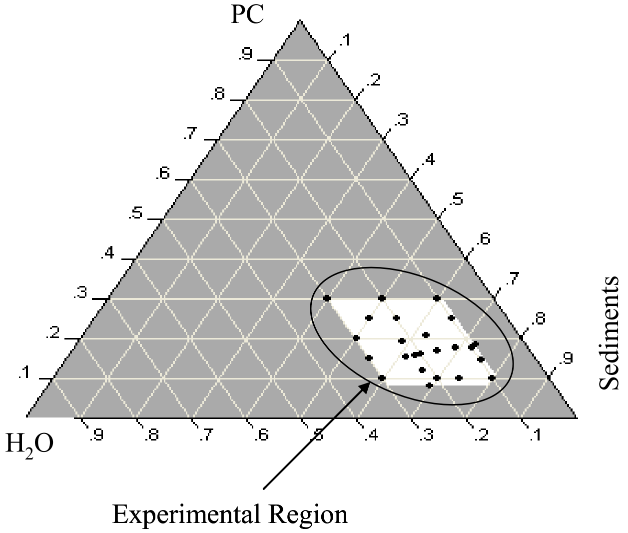


FIGURE 1. Ternary plot of mixture space with experimental region.

RESULTS AND DISCUSSION

Optimization of Process and Key Parameters

For effective carbonation of the material several factors were taken into consideration. These factors are water content, binder content, time of carbonation, method of carbonation etc. Some laboratory/small scale experiments were performed for the optimization of process and key parameters.

Water Content. Water is a medium for the carbonation to take place. Too little water prevents the reaction from taking place while too much water can block the pores between the material, acting as barrier to the diffusion of CO_2 thus decreasing carbonation. Hence there is a need of optimum water content. Optimum water content differs with material. Variation of % $CaCO_3$ obtained with respect to water content is shown in Figure 2. It can be seen that for the mixture of sediments and Portland cement (10%) optimum water content ranges between 20% and 22%. With the increase in water content reduction in CO_2 uptake can be seen thereby reducing $CaCO_3$.

Binder Content. Different types of binders can be used, like Portland cement (PC), lime, CFA, CKD etc. In this research Portland cement was used as a binder as it has better potential of carbonation. As the percentage of binder is increased amount of % $CaCO_3$ is also increased. However, at certain point, addition of binder shows less significant difference in the increase in % $CaCO_3$ (See Figure 3). It can be seen from figure 3, there is not significant difference between $CaCO_3$ obtained for 25 % PC content and 30% PC content. Therefore considering the lower limit PC content was restricted to 25 %.

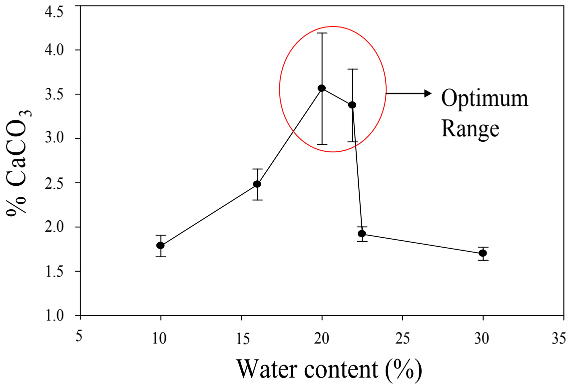


FIGURE 2. Effect of water content

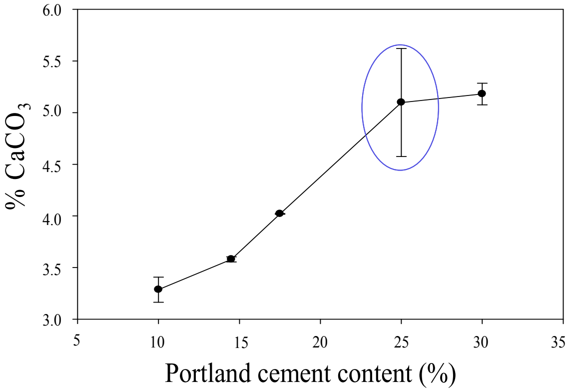


FIGURE 3. Effect of PC content

Time of Carbonation. Time of carbonation controls the percentage of material reacted (Bukowski & Berger 1979), although rate of carbonation may decrease with the progress of reaction (Berger & Klemm 1972). As seen in Figure 4, during first 2 hours of carbonation there is a drastic increase in percentage of $CaCO_3$. However, after 2 hours of carbonation mixture/material is incapable to intake more carbon dioxide hence stabilizing the process of CO_2 sequestration.

Method of Carbonation. As it was mentioned earlier, carbonation was done in both a tumbler and a column. The TGA plot (Figure 5) shows comparison between both the processes. However, no significant difference in both the processes can be seen. More material can be carbonated in tumbler at a time and thorough mixing of material with CO_2 can be achieved. TG analysis indicates a peak between 550°C and 950°C on the basis of CO_2 evolution which is associated with $CaCO_3$.

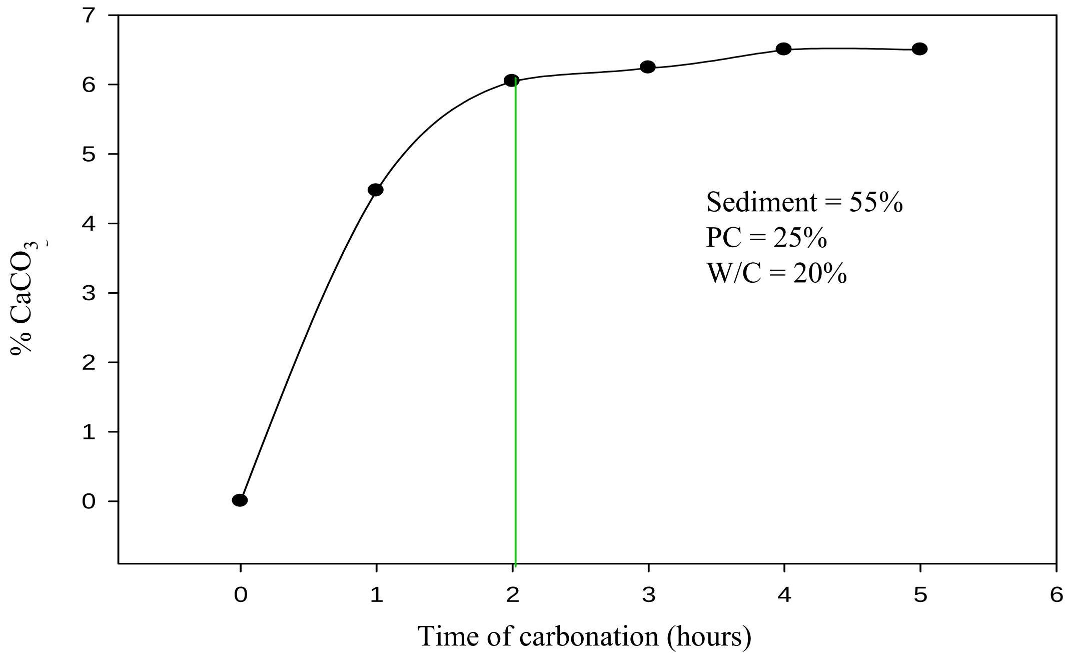


FIGURE 4. Variation in % $CaCO_3$ obtained with time of carbonation

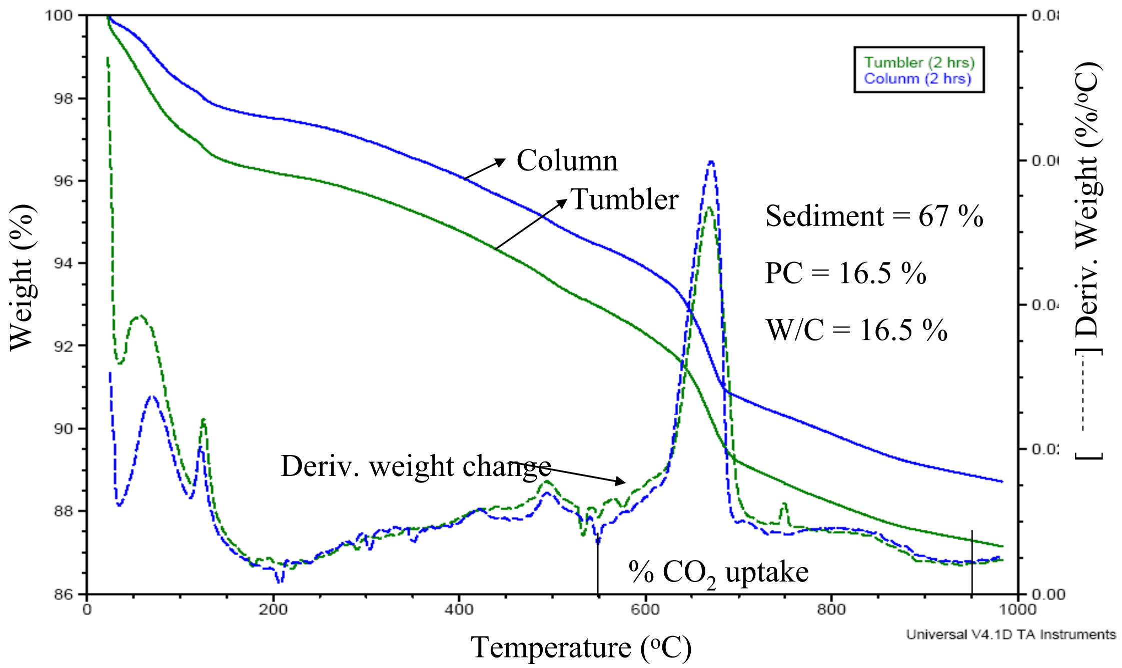


FIGURE 5. TGA graph showing comparison between Column carbonation and Tumbler carbonation

Full Scale Experiments. Using a mini concrete mixer, full scale experiments were conducted on the optimum mixture obtained from small scale experiments. Sieve analysis was performed in which it was observed that around 90-95 % aggregates fall under gravel category (≥ 4.75 mm). When these aggregates were cut in half two distinct layers were visible showing carbonated cover zone and uncarbonated core zone (See Figure 7).

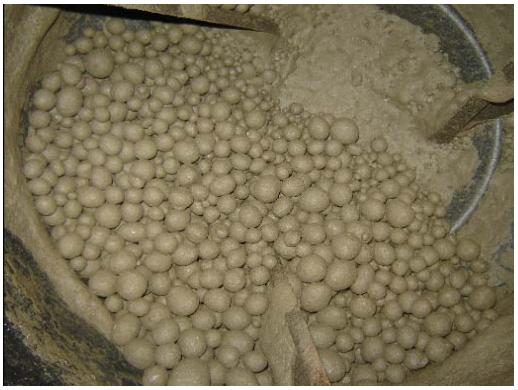


FIGURE 6. Artificial Aggregates in mini concrete mixer

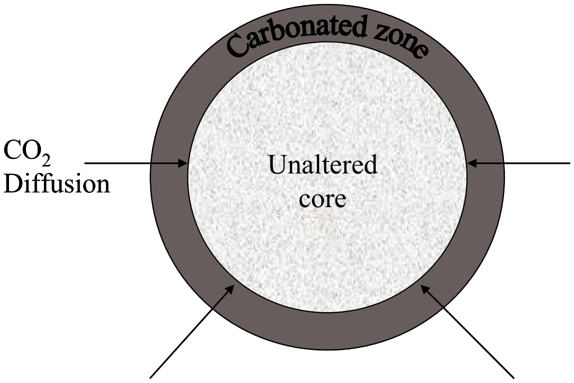


FIGURE 7. Schematic of diffusion of CO_2 in Artificial Aggregate

Furthermore, in order to confirm the irregular diffusion of CO_2 into aggregates, TGA and SEM analyses were performed. Figure 8 shows a graph of variation in $CaCO_3$ over increasing diameter of aggregate. It can be seen that, with the increase in diameter of aggregate, diffusion of CO_2 in the core was decreased. For larger aggregates, percentage of $CaCO_3$ varies greatly between core and cover of aggregate. To ensure the presence of calcium carbonate binding the sediment particles in the aggregate, SEM analysis was carried out. Needle shape granular-textured calcite crystals were seen during SEM analysis. SEM images of cover and core zone supported the non-uniform diffusion of CO_2 (See figure 9).

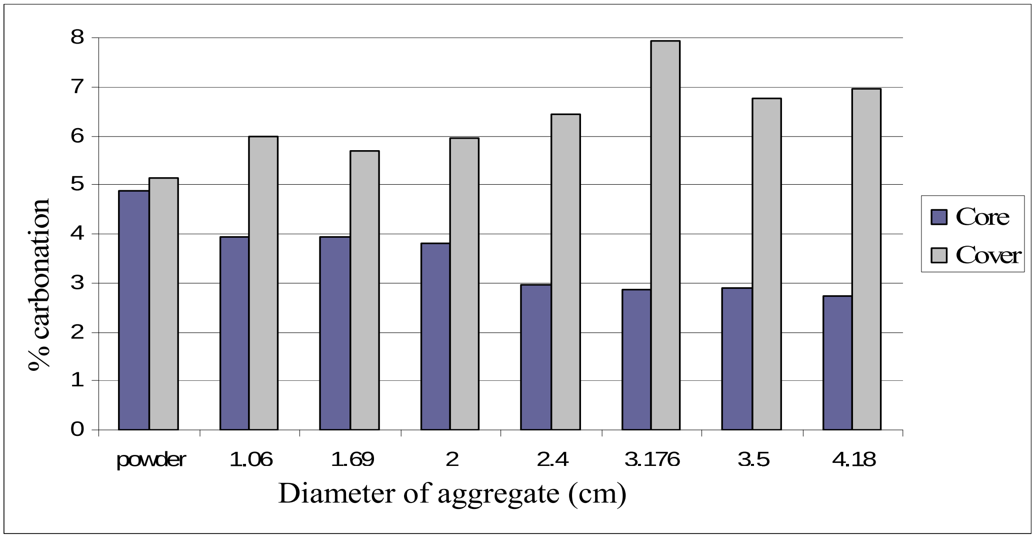
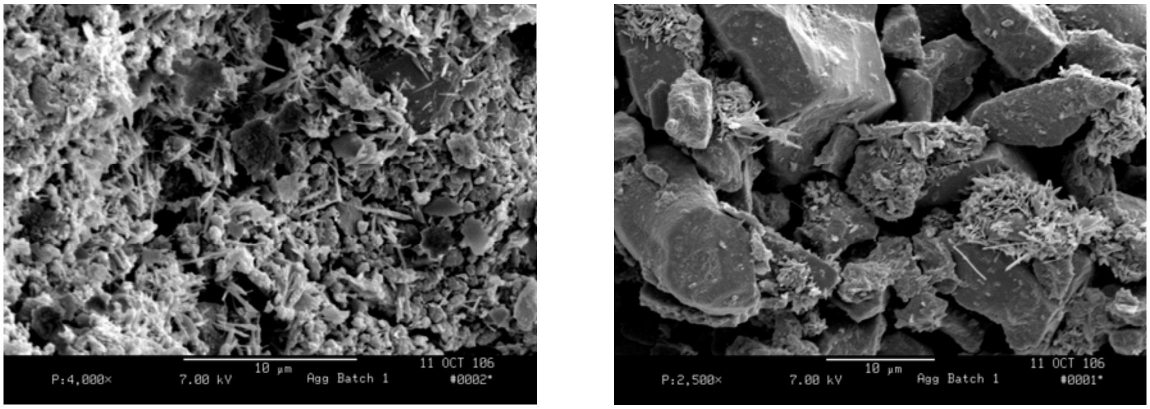


FIGURE 8. Extent of carbonation depth in core and cover of Artificial Aggregate.



(a) **(b)**

FIGURE 9. SEM images of needle shape calcite crystals in cover (a) and core (b) of aggregate

CONCLUSION

It has been demonstrated that accelerated carbonation is one of the potential treatment to treat contaminated soils. The carbonation of waste materials can occur environmentally however the rate will be very slow, whereas accelerated carbonation helps for rapid reaction of calcium phases of cement resulting in achieving high early strength than natural carbonation/hydration.

Artificial aggregates produced from full scale experiments are currently being evaluated for improvement of strength and immobilization of contaminants. If artificial aggregates meet the requirements of solidified/stabilized material, further experiments can be performed using other forms of recycled materials like CFA, CKD, stainless steel slag etc. Recycling the waste in the form of artificial aggregates can resolve some of the environmental related issues, like utilization of dredged sediment in positive way, reduction of CO_2 by sequestration, improvement in heavy metal retention in contaminated sediments and to some extent fulfilling the demand of natural aggregates i.e. use of artificial aggregates as a filling material.

FURTHER WORK

From the work done on laboratory scale experiments, parameters controlling carbonation of sediments were identified. Applying all the governing conditions including process optimization, successful production of artificial aggregates was achieved. Further work involves checking suitability of these aggregates in highway environment. Physical properties of artificial aggregates such as gradation, Atterberg limits, compaction, CBR and uniaxial compression testing is in progress. The final aim of this research is to use contaminated sediments in beneficial use application; hence this research can not be completed without testing these aggregates for their leaching potential. pH dependent leaching test is being carried out for the Gowanus canal sediments before treatment and after treatment with accelerated carbonation.

ACKNOWLEDGMENTS

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