

Utilization of Coal Combustion Byproducts as Capping Amendments for Heavy Metals Sequestration

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INTRODUCTION

Metals and metalloids are natural earth elements that are used in a variety of human activities. They cannot be degraded or destroyed. Among the most toxic heavy metals are lead (Pb), cadmium (Cd), arsenic (As), mercury (Hg), and chromium (Cr). Their common uses are: As for wood preservation; Cd for batteries, pigments, metal coatings, and plastics; Cr for making steel and wood preservation; Pb for production of batteries and ammunition. These metals present a great pollution threat because of their long life span, toxicity, and ability to bioaccumulate. Examples of their health effects on humans are kidney and liver damage (Cr), chronic damage to the nervous system and reproductive system (Cd), congenital malformation (Hg), and cancer (As).

Sediment contamination in estuarine and coastal regions is widespread in the world. Contaminated sediment is soil, sand, organic matter, or other minerals that accumulate on the bottom of a water body and contain toxic or hazardous materials at levels that may adversely affect human health or the environment (USEPA, 2006). It may be present in wetlands, streams, rivers, lakes, reservoirs, harbors, along ocean margins, or in other water bodies. Contaminants can be transported into the overlying water column by advective and diffusive mechanisms. A way of controlling this is through in-situ capping.

The concept of in-situ capping consists of the placement of an underwater covering of clean material over the contaminated sediment that remains in place, thus minimizing contaminant release into the water body (Jacobs and Forstner, 1999). In-situ caps generally reduce risk through three primary functions: physical isolation, stabilization, and reduction of contaminant transport. A well-designed and well-placed cap should more quickly reduce the exposure of fish and other biota to contaminated sediment as compared to dredging, as there should be no or very little contaminant residual on the surface of the cap. Also, the cap often provides a clean substrate for recolonization by bottom dwelling organisms.

AES Company produces manufactured aggregate (MA) AGREMAX which is a mixture of fly ash, bottom ash and water. Manufactured aggregate was chosen in this study as the active cap amendment. In this study, results are presented for the performance of MA as a potential separator of the heavy metals from biota at the sediment-water interface and for isolation of the heavy metals from the overlying water.

GOALS AND OBJECTIVES

This project is to investigate the feasibility for enhanced in-situ capping of heavy metals in marine sediments through use of low-cost, industrial byproduct MA as the cap amendment to separate and sequester the heavy metals and reduce bioavailability. The overall objective of this project is to develop a low-cost in situ cap amendment for enhanced separation and decreased bioavailability of hazardous heavy metals in sediment. Additional effort is also being developed to optimize the system with respect to the amount and depth of MA and the configuration of capping layout. Results from in situ MA-aided capping were compared to those from typical passive in situ capping with the sand layer alone.

MATERIALS AND METHODS

Capping Amendment Material Characteristics

Sieve analysis was made to characterize the MA used for the experiment. First the MA was oven-dried in order to remove humidity that did not permit it to be crushed. Later, the MA was broken down using a crusher in order to obtain smaller, more useful material. Finally, sieve analysis was made using sieve numbers 4, 8, 10, 18, 40, and 200. Only material retained up to sieve number 18 was used. Reason for this was because smaller materials had shown to create high turbidity in water. Also, smaller materials promoted fugitive dust. This resulted in the use of 66% of total MA crushed.

Artificial Contamination of Sediment

The contaminated sediment was artificially made in the laboratory using a clayey soil collected from Isabela, P.R. The main reasons of the selection of these materials were that it had been well characterized in our laboratory, it was abundant and easily available, and it was environmentally clean.

Equal volumes of 50 mL of each heavy metal at a concentration of 1000 ppm in 2% (v/v) HNO₃ was mixed into 20 L of water and blended with 850 in³ of Isabela clay. Two electric mixers were used to blend the mud for 6 days to provide an equilibrium time. After this, clay was left to settle for 1 day. Remaining solution was drained out (about 15 L).

Reactor Setup

The experimental set up consists of 4 reactors; one control and three different treatments. Table 1 shows the amount of materials in each reactor.

Table 1. Amount of materials in the reactor

TANK	Contaminated Sediment		AGREMAX® Layer		Sand Layer	
	Lb	kg	lb	kg	lb	kg
Control (R1)	7.44	3.39	0.00	0.00	18.18	8.23
Reactor 2	8.32	3.77	3.98	1.81	16.50	7.50
Reactor 3	6.96	3.15	5.06	2.30	16.89	7.68
Reactor 4	2.06	0.93	3.71	1.69	16.27	7.40

A motor with four pump heads applied a constant flow (1.7 mL/s) through the same length of Nalgene® tubing to the reactors. A pH meter and a thermometer were used to monitor basic water quality in the reactors. Reactor configurations were as shown in Figure 1.

Reactors set up.

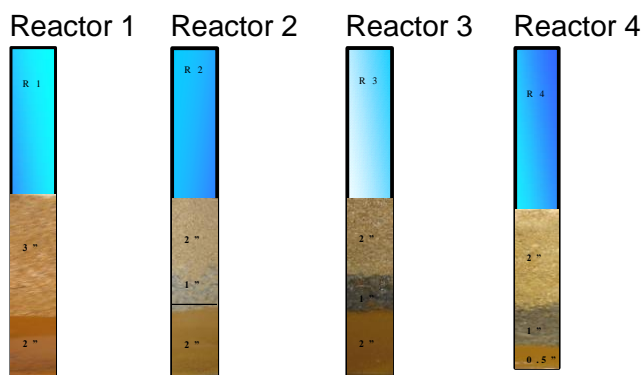
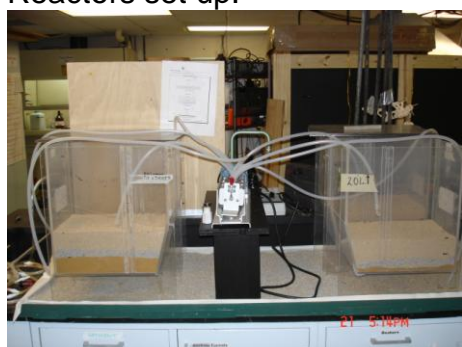


Figure 1. Reactor configuration.

Control (Reactor #1)

For the control (R1), the first layer (starting at the bottom) was comprised of contaminated sediment. The second layer contained the manufactured aggregate AGREMAX® (capping amendment) in the designed amount of 1 inch. A third layer with sand was used as the final capping layer. A water column was present on the top.

Reactor # 2

For the Reactor #2 (R2), the following scenario was prepared. A layer of contaminated sediment had a height of two inches. Biopolymer chitosan was inserted between this layer and the next one. In this study, chitosan polymer was used to evaluate its contribution as an additional capping amendment, contrasting with capping configurations of the other reactors. It was chosen because it has shown great removal efficiency in the treatment of heavy metal containing solutions. A layer of AGREMAX

was then placed with a height of 1 inch. Finally 2 inches of sand were placed. Water column lied on top.

Reactor #3

The third Reactor (R3) contains 2 inches of contaminated sediment on the bottom, followed by 1 inch of AGREMAX , and finished with a top 2 inch layer of sand. This scenario was to assess AGREMAX ® as the only altered variable of the system. The 1-inch layer of the MA was to reduce the amount of sand, but provide the same transport distance in order for the contaminants to reach aqueous layer.

Reactor #4

The configuration for this reactor followed the same as for Reactor #3, except that it consisted of 0.5 inches of the contaminated sediment (not 2 inches). This reactor presents a change in the ratio of AGREMAX to contaminated sediment compared to those for other reactors. All tanks were filled with 15.0 L of tap water. In contrast to the previous three scenarios, no flow was applied to this system (i.e., batch mode). An unexpected situation has arisen during the run of the Reactor #4; it started leaking slowly from the bottom. However, advantage of the situation was taken. The leaking water has been collected and analyzed.

ANALYSIS

Sampling

At each sampling event, 25 mL was sampled from the Reactors #1, #2 and #3. Also, equivalent amount of leaked water was sampled from Reactor #4. Each sample was pretreated to contain a 2% HNO₃ concentration to preserve the materials of interest and to meet the ICP-OES requirements. Sampling was made at alternative days starting February 27, 2007. If a sample time was missed, the next day sampling was conducted and continued the routine from there on. Samples were taken using a micropipette.

Heavy Metal Detection and Quantification

Inductively Coupled Plasma Mass Spectrometry (ICP-OES) is a very powerful tool for trace elemental analysis of heavy metals. In this study, the aqueous concentrations of the target heavy metals Pb, As, Cd, and Cr were quantified via ICP-OES analysis during the time course of the experiment.

Safety Control

Proper garments and equipment were used at all times: lab coat, gloves, safety eyeglasses, and mask. All disposable material that came, or may have come, in contact with heavy metals was properly disposed of in a designated isolated waste container. Due to concern for possible reactor leakage, a safety box was constructed and filled with absorbing material and an impermeable film to prevent further spreading.

EXPERIMENTAL RESULTS

Two calibrations were made with the ICP-OES. The first calibration was done to verify Limit of Detection (LOD), Limit of Quantification (LOQ), and machine response. LOQ and LOD were found to be 0.0384 ppm and 0.0128 ppm, respectively. After scanning for different system lines, it was found that due to damage of first line of the ICP-OES; only Cd could be analyzed for now. The first calibration proved successful with a correlation coefficient (R²) of 0.9998. The second calibration was used for sample analysis with a satisfactory R² of 0.9999. LOQ and LOD obtained are 0.0792 ppm and 0.0294 ppm, respectively. These values were very acceptable for our analysis.

Up to date, no presence of Cadmium has been detected in the aqueous layer. Cadmium has, however, been detected in Reactor #4's water leaked from the bottom as shown in Figure 2. This was expected since the water leaking comes from the contaminated sediment layer. Since heavy metal release from the sediment was expected to occur through a slow diffusive mechanism, a longer time span would be taken. Therefore, a long term monitoring was promptly planned.

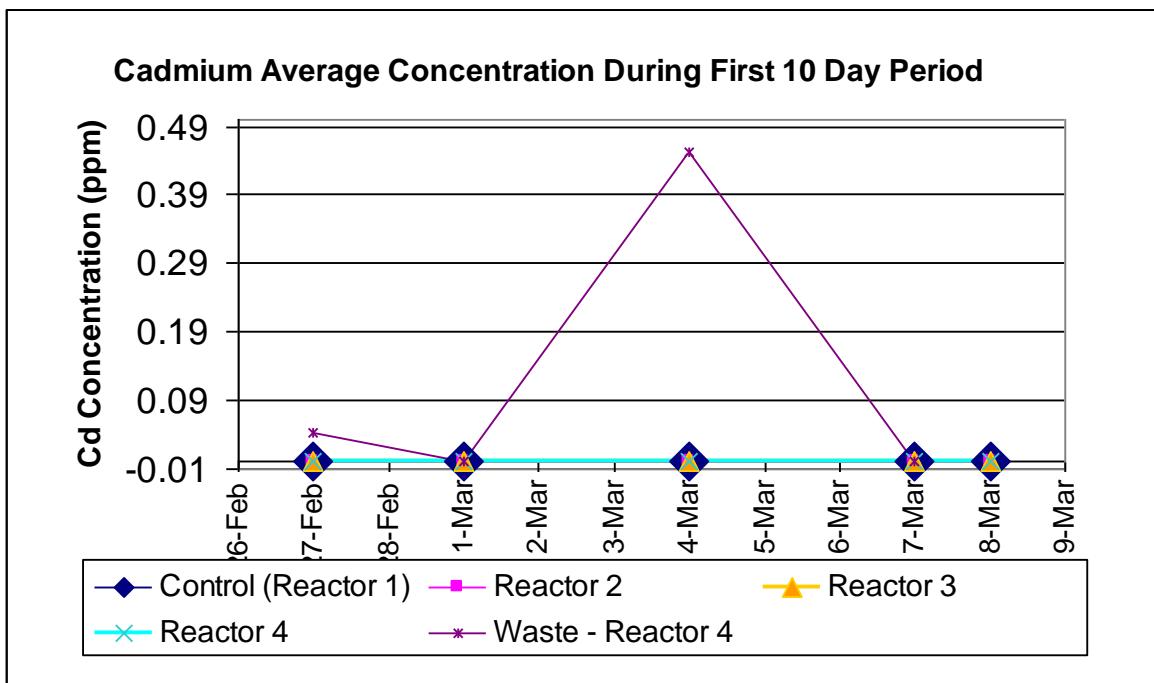


Figure 2. Concentrations of cadmium in overlying water.

CONCLUSIONS

According to the results obtained, the MA is working as a good capping material since no Cd has been detected yet in the overlying water. Due to the slowness of diffusion, a longer time span of analysis is recommended in order to ensure to quantify

effectiveness of MA as in situ capping amendment for heavy metals. Analysis for other heavy metals (Pb, As, Cr) has been seeking in many other alternative ways. Results will be obtained before reaching definite conclusions derived from the current project.

The use of the manufactured aggregate AGREMAX® for in-situ capping purposes not only provides a way to remediate contaminated sediment with heavy metals, but also offers a means of reutilization of industrial byproducts that has been produced for years for the sake of electricity generation.

REFERENCES

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