

Design of In Situ Caps for the Isolation of Contaminated Sediments

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Abstract

Formulations of bentonite-cement composites are explored as a basis for creating a range of structured, semipermeable layers adapted to *in situ* capping of contaminated underwater sediments. In addition to being mechanically stable, such composites provide for a possibility to control cap microstructure and transport properties through the fine-tuning of postdepositional hydration processes in the cap. Microscopic studies combined with flowability and setting tests were used to establish relationships between the structure and mechanical properties for designed composites. Also, apparent diffusion coefficients were measured and corresponding porosity values were calculated for the composites formed under different hydration conditions. It is demonstrated that by varying the cement content and liquid-to-solid ratio during composite formation, it is possible to control structural and transport characteristics of the composite material. Analysis of calculated porosity values combined with microscopy data indicates that the particle packing density plays a crucial role in the development of cap's microstructural features and retardation capacity.

1. Introduction

In situ capping involves the placement of a subaqueous covering or cap of clean isolating material over contaminated sediment¹. This approach to mitigating risks

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¹ Palermo, M. R., S. Maynard, et al. (1998). Guidance for in-situ subaqueous capping of contaminated sediments. US EPA.

associated with contaminated sediments has been implemented at numerous sites in the United States² and other countries^{3,4,5,6,7,8}.

Two of most important functions that an *in situ* cap must perform are to retard the release of contaminants to the overlying water column and to physically stabilize the contaminated sediment materials. The primary design variables for sediment caps have been largely limited to the choice of materials, their spatial distribution within the cap, and the cap thickness. Capping materials typically used include quarry sand, natural sediments, or soils. Although these materials may often be convenient from the standpoint of availability, their heterogeneous nature may limit the range of physical and chemical properties achievable in the final cap. In addition to a consideration of cost, choices for materials are typically made based on the physical and chemical properties of contaminated sediments, local hydrodynamic conditions, potential for consolidation of the cap and underlying sediments, and potential for bioturbation of the cap by benthic organisms⁹. Materials such as Aquablock™, zero-valent iron, apatite, and BionSoil™ have been proposed to create reactive cap barriers and, in some

² Bokuniewicz, H. J., J. Gebert, et al. (1978). Field study of mechanics of the placement of the dredged material at open-water disposal sites. Dredged material research program}. U. A. E. W. E. Station.

³ Division, E. (1991). The inhibitory effect that sand capping has on the release of nutrients from underlying sediment and the estimation of the sedimentation velocity of fresh deposits (Interim Report). Otsu, Japan, Department of Civil Life and Environment, Shiga Prefectural Government.

⁴ Instanes, D. (1994). Pollution control of a Norwegian fjord by use of geotextiles. 5th International Conference on Geotextiles, Geomembranes, and Related Products, Singapore.

⁵ Azcue, J. M., A. J. Zeman, et al. (1998). "Assessment of sediment and pore water after one year of subaqueous capping of contaminated sediments in Hamilton Harbour, Canada." *Water Sci. Technol.* **37**(6-7): 323-329.

⁶ Bona, F., G. Cecconi, et al. (2000). "An integrated approach to assess the benthic quality after sediment capping in Venice lagoon." *Aquatic Ecosystem Health and Management* **3**: 379-386.

⁷ Palermo, M. R., J. E. Clausner, et al. (1998). Guidance for subaqueous dredged material capping. U. A. E. W. E. Station. Report DOER-1.

⁸ Zeman, A. J., S. Sills, et al. (1992). *Subaqueous Capping of Contaminated Sediments: Annotated Bibliography*. NWRI Contribution No. 92-65. Imprint: National Water Research Institute, Burlington, Ontario.

⁹ Work, P. A., P. R. Moore, et al. (2002). "Bioturbation, advection, and diffusion of a conserved tracer in a laboratory flum." *Water Resources Research* **38**(6): Art. No. 1088.

cases, caps made using these material have been demonstrated to perform better than those made from conventional materials^{10,11}.

In this paper, we evaluate the use of bentonite-cement composites to achieve post-depositional control by varying conditions for cement hydration and the concomitant pore space evolution. We hypothesize that the microstructure and transport properties of bentonite-cement composites can be controlled using liquid-to-solid ratio and cement fraction as parameters. Bentonite is chosen as a well characterized model compound simulating low organic content clayey soil. The bentonite-cement composite cap design problem is formulated as optimization of the cap composition and cap placement protocol to achieve a mechanically stable, controlled porosity cap. Experimental variables in our laboratory scale experiments are a) liquid-to-solid ratio, b) cement fraction in the composite and 3) the duration of mixing before pumping the cap material into water at some elevation above the contaminated sediment. We use SEM imaging to obtain information on the structure of such caps, while strength and flowability tests were used to evaluate mechanical properties of the cap. We combine measurements of mechanical properties with microscopic imagery to establish a structural basis for the strength development observed in these materials. To further test the hypothesis, we carry out a series of diffusion experiments where the transport of non-reactive tracer is driven by a concentration gradient across a thin sample of bentonite-cement caps of different liquid-to-solid ratios and cement fractions. By comparing experimental data with model predictions, we obtain apparent diffusion coefficients as characteristics of the retardation factor for the composites. Further, from diffusion coefficients we calculate cap porosities and combine this information with structural data to understand how the microstructure of composites develops. We compare transport properties of bentonite-cement caps of different composition to better understand principles that govern the evolution of composite microstructure and how the microstructure and transport properties of such composites relate.

MATERIALS AND METHODS

Cap Preparation

¹⁰ Hull, J. H., J. M. Jersak, et al. (1999). In situ capping of contaminated sediments: comparing the relative effectiveness of sand versus bentonite-mineral based sediment caps. 1999 Conference on Hazardous Waste Research.

¹¹ Reible, D. and W. D. Constant (2002). Comparative validation of innovative capping technologies. "Active capping". Anacostia Watershed Toxics Alliance update.

A total of six cap preparations were evaluated with cement fractions varying from 10 to 50% (Table 1). In addition to varying cement content, capping materials varied with respect to the amount of water added to the cement/bentonite mixture. Caps were prepared by mixing cap components with an amount of water calculated based on an operationally defined "water demand" for the combined mixture. Water demand values of 1.832 g(water)/g(bentonite) and 0.303 g(water)/g(cement) were defined as the amount of water added to a dry sample of clay or cement until the absorptive capacity was reached and excess water appeared on the sample surface within 2 minutes. The water demand for a given mixture of clay and cement was taken to be the mass-weighted sum of the individual demands for the clay and cement. Caps were prepared by adding 1.5 times more water than these operationally defined demands to ensure a flowable material. The slurries were then mixed for approximately 15 min to promote carbonation¹².

Diffusion Tests

Using chloride as a tracer, diffusion tests were performed with a modified diffusion cell¹³ (Figure 1). Modifications allowed for higher closed-circuit cross flows, pump pulse dumping section at the entrance, and sampling ports to monitor contaminant depletion in the contaminated sediment. Sampling ports were plugged with Thermogreen (LB-1, cat. no. 20668, Sigma-Aldrich) septa. All but the upper 16 mm of the bottom portion of a T-shaped Plexiglas cell was filled with glass beads 1 mm in diameter (A-series glass beads, cat. no. A-090, Potters Industries, Inc.) and 20 mg/L NaCl solution simulating contaminated sediment. Upper portion of the cell constituted the flume simulating the water flow above the capped sediment. The inlet part of the flume, separated by a plastic mesh, was filled with 5 mm glass beads (cat. no. 11-312C, Fisher Scientific) to dampen pulsation of the peristaltic pump and to distribute the inflow over the entire cross-section of the flume. The outlet opening was protected by plastic mesh patches (41×41 openings per cm², cat. no. 9318T18, McMaster-Carr) to keep occasional particles from entering the pump part of the loop and piercing the elastic tubing. Peristaltic pumps (Masterflex model no. 7553-70, (6 to 600) rpm, Cole-Parmer) with two heads (Cole-Parmer, cat. no. U-07013-05) mounted on each were used to circulate the water above the caps in simultaneously operated cells at the rate

¹² Taylor, H. F. W. (1997). Cement Chemistry. London, Thomas Telford.

¹³ Wang, X. Q., L. J. Thibodeaux, et al. (1991). "Efficiency of capping contaminated bed sediments in situ. 1. Laboratory-scale experiments on diffusion-adsorption in the capping layer." Environ. Sci. Technol. **25**: 1578-1584.

of 0.324 mL/s, which translated to the cross flow velocity of 0.147 mm/s. Conductivity and temperature of the flume water was measured using combination chloride-

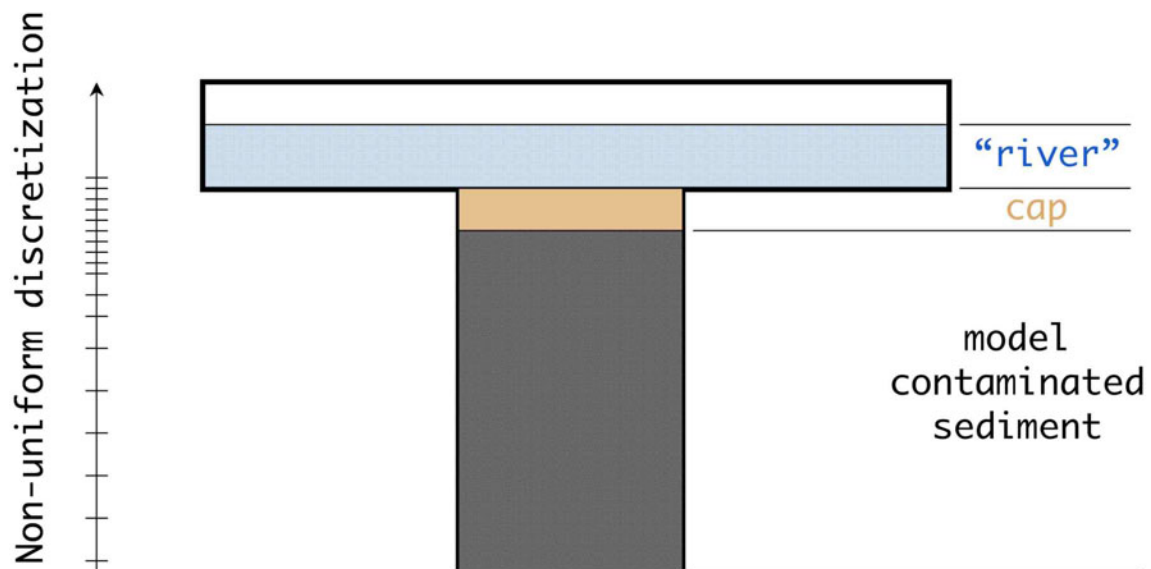
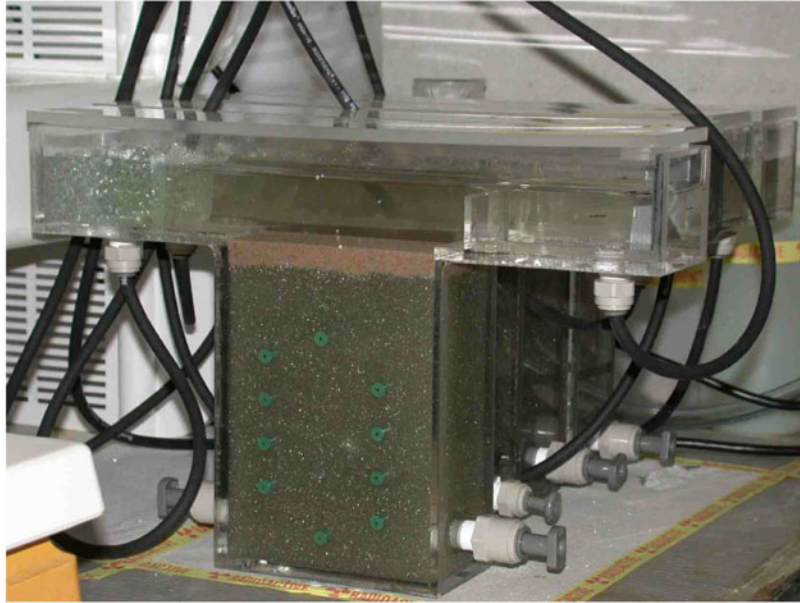


Figure 1. Diffusion cell: photograph of several cells operated simultaneously (upper image) and conceptual diagram of the cell (lower image).

selective electrode (cat. no. A-27502-13, Cole-Parmer) and conductivity meter (model 1671, Jenco Electronics Ltd.) calibrated using calibration standards (cat. no. A-27502-63, Cole-Parmer). From the volume of the water lost from the upper compartment of the cell, the evaporation rate was calculated.

Cap materials were mixed at a given proportion and at given water content for 15 min and then placed over the model sediment to fill the remaining 16 mm of the bottom portion of the T-shaped diffusion cell. The upper compartment of the cell was purged with deionized water for 10 min to remove residuals of the model "contaminant" (chloride), which could be introduced during the cap placement stage. 10 mL aliquots of the solution circulated above the caps were taken periodically to determine the concentration of chloride in the upper compartment of the diffusion cell. At the end of each experiment, chloride concentration profiles in the model sediments were recorded by sampling through 11 septa ports in the diffusion cell. Only 10 ports are depicted in Figure 1; after the picture was taken, the eleventh port was added between the upper port and the cap. Samples of approximately 1 mL volume were diluted by Millipore water to approximately 50 mL and chloride concentration was measured using a chloride selective electrode (cat. no. 27502-12, Cole-Parmer).

Experiments on diffusion through a porous medium of known characteristics (a glass bead cap) were performed first to estimate the molecular diffusivity D_{aq} of chloride in water. The porosity of the glass bead cap was measured experimentally. Due to the well defined pore geometry of this cap, the tortuosity could be estimated with a high degree of confidence using (2) and the value of $m = 1.5$ in the tortuosity-porosity relationship. The obtained value of D_{aq} was used then in the finite differences diffusion model to compute apparent diffusion coefficients, D_{app} , for all other cap materials studied in this work.

In interpreting results of experiments with bentonite-cement composite caps, D_{app} was used as a fitting parameter to fit model prediction to experimental data. From the D_{app} value resulting in the best least square fit and from the D_{aq} estimated as described above, the cap porosity was computed. The value of $m = 4/3$ in the tortuosity-porosity relationship (2) was used in calculations.

Numerical Modeling

To model the diffusion across caps, finite differences numerical model was developed. Non-uniform discretization was employed to solve the problem more efficiently while accurately representing the steepest concentration gradients present in the system. The higher the non-uniformity of the grid is, the less accurate these approximations become: first derivative and second derivative approximations become less than second-order and less than first order accurate, respectively. To represent the stepwise change in the diffusion coefficient at the sediment-cap and cap-water interfaces, central difference

scheme incorporating two diffusion coefficients was derived and used to solve the diffusion equation. At the boundary, the upwind scheme was employed, while the central differencing was used in the rest of the computational domain as there was no advection term and, therefore no preferential direction.

From the value of flux at the cap-water (c-w) interface calculated using Fick's first law, the accumulated concentration was computed for the upper ("water") compartment of the cell and used to determine the concentration at the cap-water interface. Evaporation and dilution due to periodic sampling were also accounted for in the model. Diffusion coefficients were calculated by minimizing the residual in the least-squares problem.

SEM Characterization of Cap Morphology

Effects of bentonite-cement ratio on the morphology of pore space in composite caps were studied using SEM and iDX elemental mapping. iDX mapping of bentonite-cement composites was carried out to estimate the elemental distribution within samples (not shown). Cement and bentonite fractions were found to be homogeneously distributed within the spatial resolution limits of the EDX method.

As in the case of hydrating neat cement, the liquid-to-solid ratio had a profound effect on the morphology of the pore space. In the CEM10 samples, the water-to-cement ratio was very high (8.5). Under such conditions, no anhydrous cement is expected to remain. The SEM imaging and EDX analysis of CEM10 samples confirmed that no cement grains were present in the composite.

In composites with a 20% cement fraction very small amounts of cement hydration products were observed. The water-to-cement ratio for CEM20 was still very high, and most of cement grains are dissolved and precipitated as hydration products.

For higher cement contents, samples with two liquid-to-solid ratios were studied. For 33% cement samples, lower water content CEM33L and higher water content CEM33H composites were investigated. In case of 50% cement composites, again samples with low and high content were studied. Hydration products of same types as those resulting from the hydration of neat cements were observed.

For both, 33% and 50% cement samples, more porous composites were formed at higher water content. Generally, such composites can be regarded as a more or less continuous skeleton of cement material (both anhydrous grains and hydration products) enclosing a clay matrix. The lack of continuity of the skeleton at lower cement contents resulted in composites that were not as strong mechanically as composites with higher cement content.

Notwithstanding the fact that at low water contents less hydration products responsible for the strength development were formed, such composite samples were stronger. This can be attributed to the fact that less CSH is necessary to bridge particles that are closer to one another. Poorly hydrated samples with cement and clay grains bridged by the CSH phase in its early development stage were stronger than overhydrated samples clay particles bridged by a tight CSH network.

Diffusion test results

Experimentally determined value of $D_{aq} = 1.43 \cdot 10^{-5} \text{ cm}^2/\text{s}$ agreed well with values of $3.04 \cdot 10^{-5} \text{ cm}^2/\text{s}$ ¹⁴, $2.01 \cdot 10^{-5} \text{ cm}^2/\text{s}$ ¹⁵, and $1.59 \cdot 10^{-5} \text{ cm}^2/\text{s}$ ¹⁶ estimated from empirical correlations for molecular diffusivity of chloride. Further, to validate our approach to the estimation of cap porosity, sand cap porosity calculated based on measured D_{app} values was compared with porosity values measured by a straightforward (and precise in the case of sand) volumetric method. A good match with the relative error of 0.2% was obtained.

The upper image in Figure 2 illustrates experimental and modeled dependencies of chloride concentration on the spatial coordinate at a fixed time moment. The lower image, on the other hand, describes the evolution of flux across the cap (one location in space) as a function of time. Small peaks in the flux curve correspond to the sampling events, when the solution in the upper compartment of the diffusion cell was diluted due to sampling. Measurements of the first type produced data that were less noisy and, for this reason, these data were used for the derivation of cap porosity values.

Table 1 summarizes results of diffusion experiments and related calculations. Initial porosity ε_{init} is calculated from the liquid-to-solid ratio, apparent diffusion

¹⁴ Wilke, C. R. and P. Chang (1955). "Correlation of diffusion coefficients in dilute solutions." *AIChE J.* **1**: 264-270.

¹⁵ Hayduk, W. and H. Laudie (1974). "Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions." *AIChE J.* **20**(3): 611-615.

¹⁶ Worch, E. (1993). "Eine neue Gleichung zur Berechnung von Diffusionkoeffizienten geloster Stoffe." *Vom Wasser* **81**: 289-297.

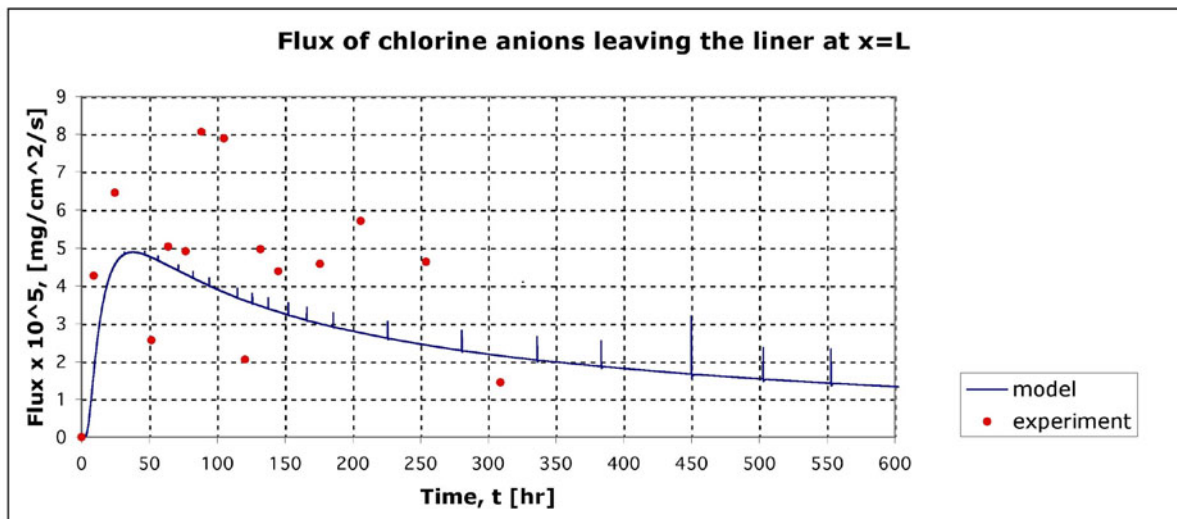
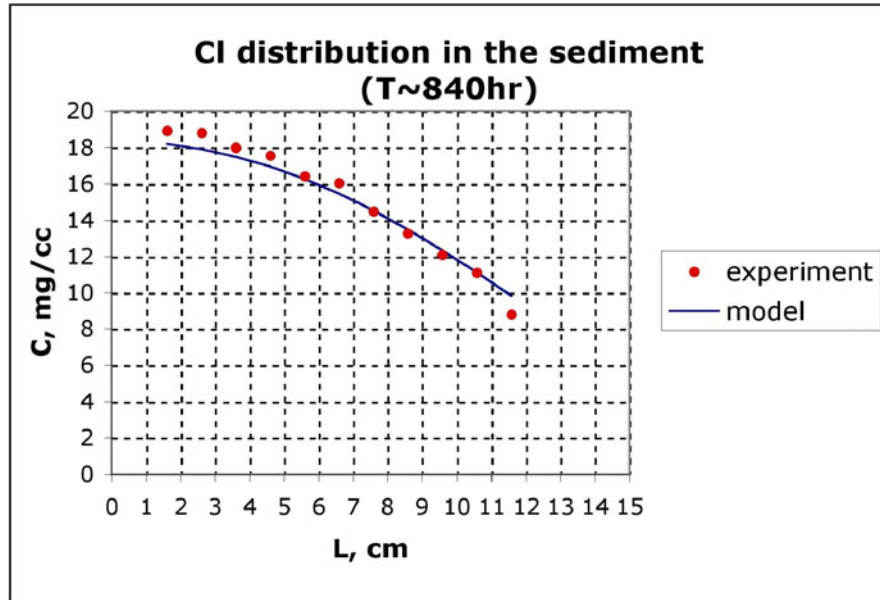


Figure 2. Experimentally determined and modeled chloride concentration profile in the model sediment after 840 hours of diffusion through the 16 mm sand cap (upper image) and time dependence of chloride flux from the sand cap into overlying water column (lower image).

coefficient D_{app} is derived by fitting modeled concentration profile in the "sediment" to the measured one, and ϵ_{calc} is computed from (5), where m was

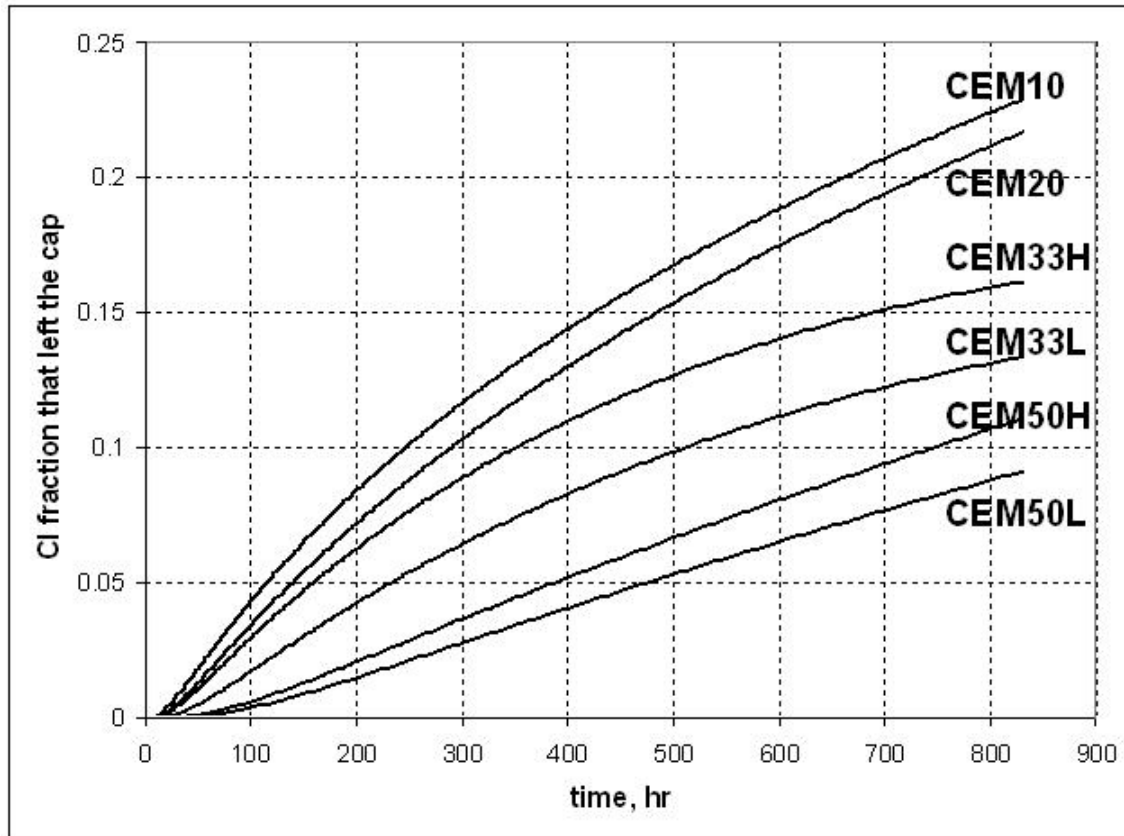


Figure 3. Fraction of chloride that left the cap as a function of time for caps different compositions

taken to be $3/2$ for glass beads and sand caps, and $4/3$ for bentonite-cement composite caps. The relative change in porosity was calculated as

$$\frac{\Delta\epsilon}{\epsilon} = \frac{\epsilon_{init} - \epsilon_{calc}}{\epsilon_{init}} \quad (9)$$

Figure 3 presents another view on the cap performance as a function of its composition.

As can be seen from the above data, the higher the cement content of a cap, the smaller the apparent diffusion coefficient and the larger the relative change in porosity. For caps with the same cement content, smaller diffusion coefficients and larger relative changes in porosity were observed for caps formed at lower

No.	Sample	Cement content	LIQUID-TO-SOLID ratio	Initial setting time, hr	Final setting time, hr
1	CEM10	10%	2.5	No	No
2	CEM20	20%	2.3	≈ 120	No
3	CEM33L	33%	2.0	≈ 17	> 350
4	CEM33H	33%	2.5	≈ 168	>400
5	CEM50L	50%	1.2	< 9	≈ 20
6	CEM50H	50%	1.6	≈ 12	≈ 30

Table 1. Initial and final setting times for bentonite-cement samples.

liquid-to-solid ratios. These observations underscore the crucial role of cement hydration in determining the microstructure and, therefore, transport characteristics of such composite materials.

A side-to-side analysis of how diffusion coefficient values obtained in this study and cap microstructure depend on cap composition leads to a heuristic description of the structure-function relationship in such materials. The final porosity appear to be the result of interplay of two factors: 1) the amount of hydration products and available host pore space in the bentonite matrix, and 2) the volume change resulting from the water addition to the dry bentonite-cement mixture. As results of diffusion tests indicate, at lower liquid-to-solid ratios, the (smaller) amount of hydration products generated in a composite during setting fills the (smaller) available pore space better than under the conditions of higher liquid-to-solid ratios.

These observations point to the importance of the closer packing of cap materials. Stabilizing the suspension of clay and cement particles that is increasing the interparticle repulsion forces may be key to achieving closer packing in the cap while still having a flowing suspension at the stage of cap placement.

SUMMARY

Bentonite-cement composite is proposed as a new capping material for the isolation of contaminated sediments. Differences in the appearance and physical properties of caps produced from variable clay/cement/ water mixtures are attributed to post-depositional chemical processes largely associated with cement hydration. We demonstrate that by varying the composition of the bentonite-cement mixture, it is possible to control structural and transport characteristics of the composite material. In particular, liquid-to-solid and bentonite-to-cement ratios are identified as experimental parameters that determine the apparent diffusion coefficient and, therefore, the performance of the in-situ cap. The particle packing density, determined by interparticle interactions in a suspension and, later, a deposit (cap), appears to control the development of cap's microstructural features and retardation capacity.