BENCH-SCALE INVESTIGATION OF THE PERFORMANCE OF SUBAQUEOUS REACTIVE BARRIERS (CAPS)

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ABSTRACT
Laboratory diffusion tests with sediment caps of different compositions were performed using 2,4-DCP (dicholorphenol) as a tracer. Higher shear strength well-hydrated clay-based caps with 10% or below cement fraction have porosity higher than that of both clay loam and sand caps. To obtain information on cap microstructure and to correlate it to the observed macroscopic transport characteristics, the methodology for the resin embedding of 100% water-saturated low permeability sediment caps for the subsequent thin-sectioning and morphological study was established. In addition, applicability of environmental SEM/EDAX for the study of *in situ* hydration of cement-clay composites was accessed. Finally, to model the cap formation process, the sedimentation/diffusion column was designed, custom-built and tested.

RÉSUMÉ
Les essais expérimentaux à l'échelle laboratoire de diffusion avec des couches de recouvrement de compositions différentes ont été conduits pour un traceur (2,4-DCP, dichlorophenol). Les couches composés d'argile et ciment (10%) caractérisés par des forces de cisaillement supérieurs, possèdent une porosité plus élevée que les couches d'argile et les couches de sable. Pour obtenir l'information sur la microstructure des couches et pour la corréler aux caractéristiques macroscopiques de transport observées, la méthodologie d'imprégnation des couches de recouvrement 100% saturées d'eau avec des polymères a été testée. De plus, l'efficacité du MEB environnemental/EDX a été évaluée pour les études d'hydratation *in situ* de composites argile/cement. Finalement, une colonne combinant sédimentation et diffusion a été mise au point pour modéliser le processus de dépôt des couches de recouvrement.

1. INTRODUCTION

The performance of *in situ* sediment caps is judged by their mechanical and transport characteristics. Although sand caps have been mostly used so far, more complex reactive barriers, such as those based on Aquabloc, zero-valent iron, apatite, BionSoil technologies perform better (Hull et al. 1999, Reible and Constant, 2002).

In this paper, we propose clay/cement composite as a new material for the isolation of contaminated sediments. Having only limited control over the depositional stage of the cap formation process, we create various cap microstructures by controlling post-depositional chemical processes in a cap. The technological appeal of this choice is due to the richness of design choices stemming from the complexity of the microstructure and strength development in cementitious materials. By judiciously choosing cement/clay and liquid /solid ratios of the composite, desired transport and mechanical properties of the reactive barrier may be attained. Controllable permeability and the capacity of cementitious materials to bind heavy metals (Conner 1989) make such barriers especially attractive.

Presented results indicate the importance of hydration process for the microstructure development in cement/clay composites and provide tentative guidelines for the design of such barriers.

2. DIFFUSION EXPERIMENTS

Using ^{14}C-labeled 2,4-DCP (Sigma-Aldrich, Lot no. 119H9406/07) as a tracer compound, diffusion tests were performed with a modified LSU diffusion cell (Wang et al. 1991). Modifications allowed for a 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 (Sigma-Aldrich, LB-1, Cat. No. 20668) septa. All but upper 9mm of the bottom portion of a T-shaped Plexiglas cell was filled with glass beads 1mm in diameter (A-series glass beads, Cat. no. A-090, Potters Industries, Inc.) and 1 mg/L 2,4-DCP solution spiked with ^{14}C 2,4-DCP simulating contaminated sediment. The concentration of the radiolabeled DCP was chosen to be 7μg/L, which is 100 times higher than detection limit of the scintillation counter (LSC, Beckman LS6500). Porosity of this model sediment was experimentally determined to be 39.8±0.8% (95% confidence value). 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 5mm 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 (41x41 openings per cm^2, McMaster-Carr, Cat. no. 9318T18) to keep occasional particles from entering the pump part of the loop and piercing the elastic tubing. Peristaltic pumps (Cole Parmer, Masterflex model no. 7553-70, 6-600 rpm) with two heads (Cole Parmer, cat. no. U-07013-05) mounted on each were used to circulate the

water above the caps in four simultaneously operated cells at the rate of 0,324 mL/sec, which translated to the cross flow velocity of 0,147 mm/sec.

Three different cap materials: sand (mesh no. 70), clay loam with 1.26% organic carbon content (Neale et al. 2000), and clay loam/6% cement (Porland cement) composite were chosen. Capping material was hydrated in the excess of water by mixing at moderate speed for 15 minutes and then placed over the model sediment to fill the remaining 9 mm of the bottom portion of the T-shaped diffusion cell. The upper compartment of the cell was purged with DI water for 10 minutes to remove residuals of the tracer compound, which could be introduced during the cap placement stage. Aliquots of the solution circulated above the caps were taken periodically to determine the concentration of the radiolabeled tracer by liquid scintillation counting. Details on sampling, measuring, and concentration calculations can be found elsewhere (Dalton 2002). Results of diffusion tests for the three materials tested are presented in Figure 1.

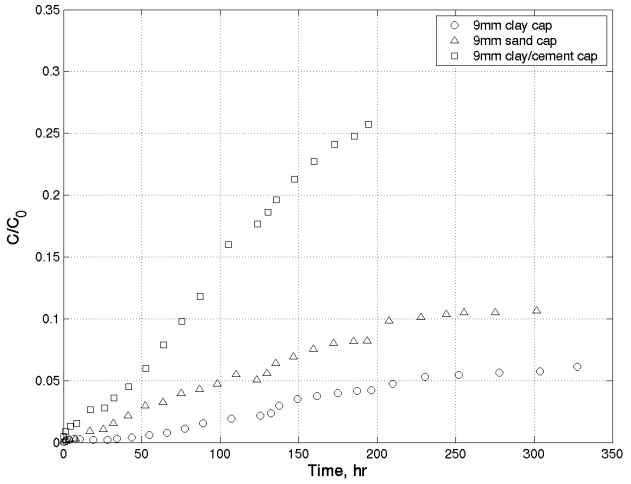

Figure 1. 2,4-DCP breakthrough curves for 9mm sand, clay loam, and clay loam/6% cement sediment caps.

Although considerably more cohesive than clay or sand caps, the clay/cement composite cap was characterized by a much higher diffusion coefficient. This was due to the higher porosity typical for well-hydrated cementitious materials. Thus, the extent of hydration appears to be the major factor determining the microstructure of such composite caps. The fact that caps must be placed underwater introduces additional difficulty for controlling the hydration of cap materials.

The cement/clay composite cap design problem may be formulated as optimization of the cap composition and cap placement protocol to achieve low porosity mechanically stable cap exerting a minimal impact on the contaminated sediments during placement. Controllable variables 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. Currently, work is I progress in our lab on the diffusion and strength testing of low porosity cement/clay composite caps.

3. MICROSTRUCTURAL STUDIES

To correlate observed macroscopic transport characteristics to the cap microstructure, information on the cap porosity has to be obtained. In this section, we describe several approaches we are taking to better understand how the microstructure develops in cement/clay composites.

3.1 Embedding and morphological study of cap structure

Two types of low-viscosity embedding media for impregnation of low permeability caps have been evaluated - epoxy resin and glycol methacrylate. Impregnation with the first medium, low viscosity (150-200 cps at 100rpm/23^{0}C) Epo-Tech 301 epoxy resin (Epoxy technology, Inc.) consisted of two steps – dehydration and embedding. During both steps, histology cells (HistoPrep tissue capsules, Cat. no. 15-182-218, Fisher Scientific) clad with fine monofilament nylon mesh (121x121 openings per cm2, McMaster-Carr, Cat. no. 9318T48) were used as sample holders to keep non-cohesive or soft cap samples from falling apart. At the dehydration stage, samples were placed into hermetically closed plastic troughs filled with 200-proff ethanol for 6 weeks. Ethanol was changed every week during the dehydration process. At the embedding stage, the dehydrated sample was placed into a polypropylene beaker (Cat. no. 02-593-50B, Fisher Scientific) with epoxy at base of the sample and then into the dessicator with drierite absorbent (Cole Parmer, Cat. no. 07-578-3B). The dessicator was evacuated to -80 kPa using the vacuum pump (Emerson. Model SA55NXGTE-4870) and then more epoxy was added to cover the sample with a 2 cm layer. The vacuum was cyclically increased and reduced during the following 20 minutes to insure there were no bubbles entrapped. The sample was then kept at 65^{0}C for 3 hours for the epoxy to polymerize. This method was found to be effective for higher-permeability samples, such as sand caps.

To preserve cap structure at the pore-scale, applying vacuum is not recommended. In this case, second medium, ultra-low viscosity (less than 1 cps) glycol methacrylate GMA “Low-acid” monomer (SPI-Chem, Inc.) was found to be more effective. The main advantage of GMA is that it is water miscible, which allows one to avoid the dehydration step, potentially damaging to the fine pore structure of samples. Cap fragments may be left for long periods of time (months) in the GMA solution for the complete infiltration. Due to it’s ultra-low viscosity, GMA may be used for the impregnation of hard-to-infiltrate samples. At the embedding stage, GMA-infiltrated samples were placed in BEEM capsules (Cat. no. 130, Pelco Int) filled with pre-polymerized GMA and were subjected to UV for the period from 24 to 72 hours in PELCO UVC2 cryo chamber (Cat. no. 6202, Pelco Int.).

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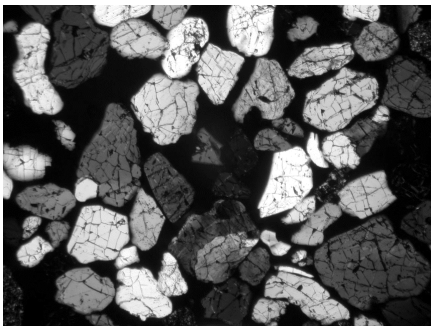

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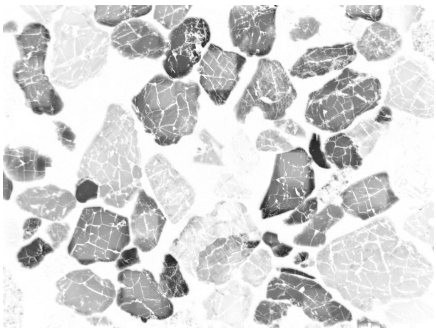

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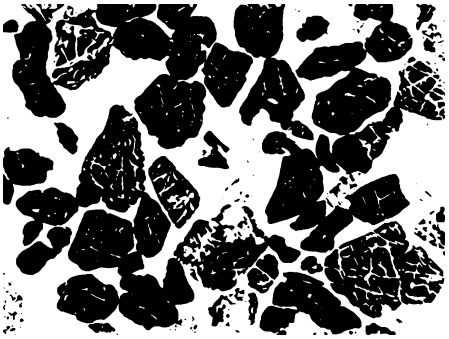

Figure 2. Image processing steps in thin-section analysis of a sand cap. a) Thin-section image in transmitted polarized light; b) same image after inversion and background subtraction; c) same image after thresholding and morphological opening

After the embedding, thin-section preparation was contracted out. No problems were reported with cutting and polishing of epoxy- and GMA-embedded samples. Polarizing light microscopy (trinocular polarizing microscope, Cat. no. ML9430, Meiji Co.) and scanning electron microscopy (FEI XL30 Schottky field-emission environmental-SEM with EDAX) were used to image 2D polished sections. Figure 2 shows steps of light microscopy imaging of a thin-section of epoxy-impregnated sand cap.

3.2 Environmental SEM for *in situ* cap hydration study

SEM in environmental mode (ESEM) allows for the examination of wet and vapor-producing samples in their native state without any prior specimen preparation (NeuBauer and Jennings 1996). In this work, ESEM has been used to study the *in situ* hydration of cements and cement-clay composites. Hydration conditions (temperature and pressure) in the ESEM chamber were identified and dynamic hydration/dehydration study was performed. Presence of clay minerals was found to significantly alter the processes of cement hydration and strength development. Figure 3 demonstrates the difference in cap microstructure as a function of cement/clay and liquid/solid ratios. In the case of a lower liquid/solid ratio (Figure 3b), one can see more anhydrous cement grains interspersed among clay platelets, while in case of a higher cement/clay ratio and

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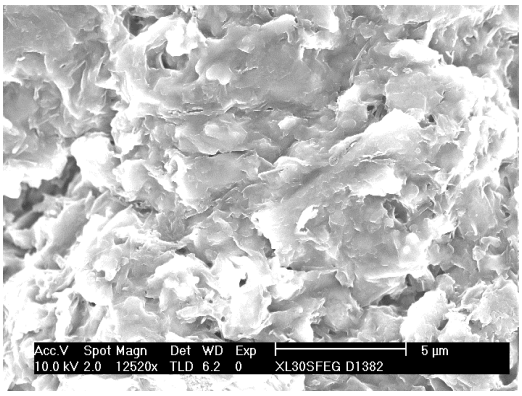

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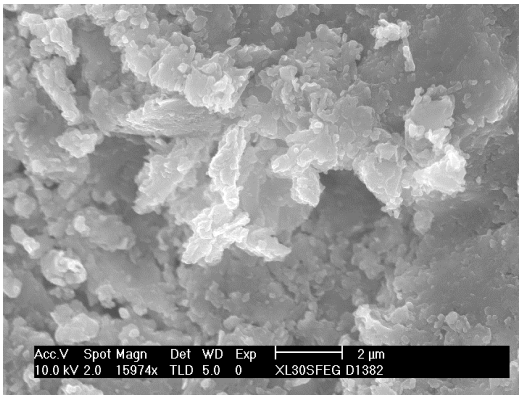

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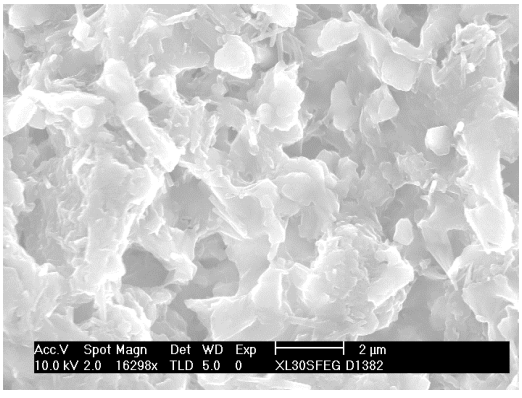

Figure 3. SEM images of cement/clay composite microstructure for various cement/clay (C/C) and liquid/solid ratios (L/S): a) C/C=1/2, L/S=3/2; b) C/C=2/3, L/S=1/2; c) C/C=2/3, L/S=3/2.

higher liquid/solid ration (Figure 3c), clay platelets appear to be covered by a diffuse layer of the amorphous CSH cement phase.

3.3 EDX elemental mapping

To analyze microstructure quantitatively, EDX mapping may be employed. By comparing chemical maps for relevant elements pore structure can be identified and used as an input to random-walk diffusion models. Figure 4 exemplifies a back-scattered electrons SEM image of a polished thin-section of a cement sample as well as several corresponding elemental maps. This work is in progress.

4. DESIGN OF SEDIMENTATION/DIFFUSION SETUP

The deposition step in the cap formation can be of critical importance for the overall performance of a reactive barrier. Settling of very dilute suspensions may lead to the over-hydration of cap materials and the formation of high porosity barriers. At another extreme, using thick slurries may results in undesirable resuspension of contaminated sediment upon impact. To model the cap deposition more realistically, we carry out settling experiments in a sedimentation/diffusion column.

Custom made Plexiglas column has been designed and built based on an existing packed bed column. The column consisted of a flat base 50x50 cm, one (lowest) cylindrical section, and four longer cylindrical sections (Figure 5). Adjacent sections were connected using 6 screws with O-rings insuring the adequate sealing. Openings at various elevations plugged with Thermogreen septa provided the opportunity to take samples of tracer solution (in the lowest section) and of settling suspension (in the higher sections) during an experiment. Most of the lowest section was filled with 1mm glass beads (A-series glass beads, Cat. no. A-090, Potters Industries, Inc.) simulating the sediment. To avoid air entrapment, the solution of a tracer solution (20mg/L of NaCl) was poured into the lowest section at the time of filling the section with beads. A wire mesh was placed on top of the model sediment and extra tracer solution was siphoned out. To prevent immediate contact of tracer-containing pore water and pure water in the above sections of the column, 80 ml volume of 1mm glass beads was filled with pure water and was placed on top of the section with the model contaminated sediment. Another wire mesh was placed on top of this layer to facilitate leveling and stabilize the layer. The rest of the lowest section left to water from syringe running down the wide spatula blade to prevent advection-induced intrusion of the tracer solution into the retardation layer. The four upper sections were mounted and pure water was pumped into them using peristaltic pump (Cole Parmer, Masterflex model no. 7553-80; pump head cat. no. U-707013-05). Very low flows directed upwards were used to fill the column next to the retardation layer. Cap material was then suspended in pure water, mixed for 3 min at 200 rpm and poured into the column. After the suspension settled, the upper three

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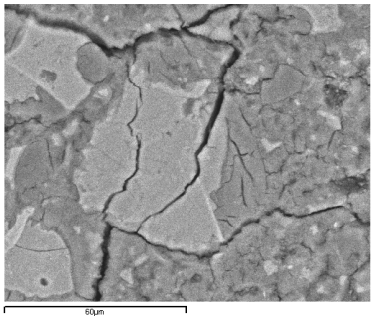

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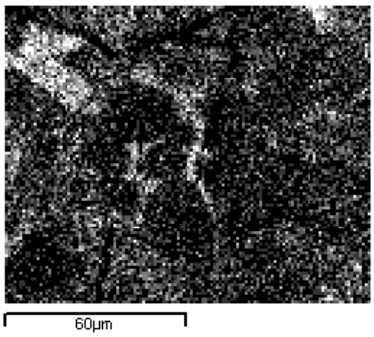

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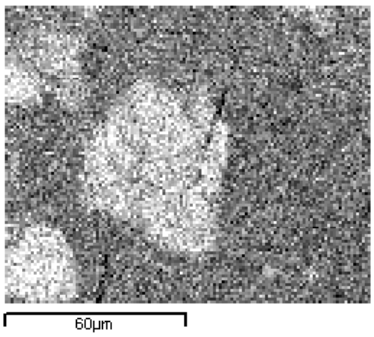

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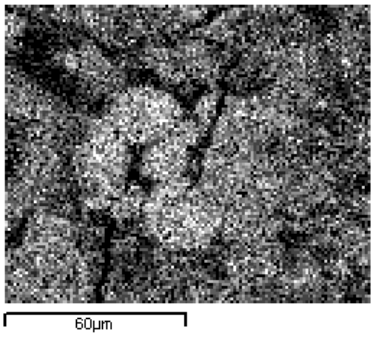

Figure 4. a) SEM back-scattered electron image of a thin-section of hydrated cement showing an anhydrous cement grain (a), and EDX elemental maps for Al (b), Ca (c), and Si (d) for the imaged area.

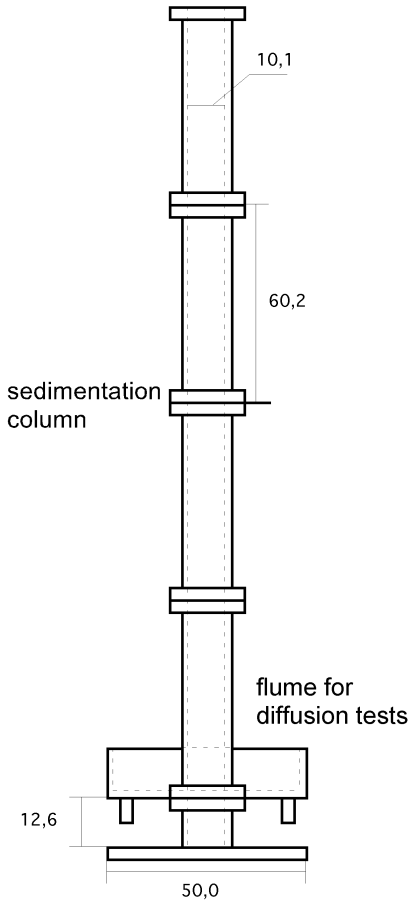

Figure 5. Illustration of a sedimentation/diffusion setup with the mountable flume (all sizes are in centimeters)

sections of the column were emptied using the same peristaltic pump and dismantled. On top of the section with the deposited cap, a custom made rectangular duct (flume) was mounted and secured with an O-ring and 6 screws. The flume measured 50 cm in length, 20 cm in width, and 10 cm in height. The space above the deposited cap was filled with DI water using syringe and spatula, ensuring the minimal disturbance of the flocculent layer on top of the accommodate the capping layer was filled with cap. Plastic mesh patches (41x41 openings per cm2, McMaster-Carr, Cat. no. 9318T18), protected the outlet opening in the bottom of the flume. The inlet part of the flume, separated by a plastic mesh, was filled with 5mm 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 section was partially separated by a 4cm high dam, which ensured the constant water level above the cap. The pumping speed was 0,324 mL/sec, which translated to the average cross flow of 0,31 mm/sec. Conductivity and temperature of the flume water was measured continuously using combination chloride-selective electrode (Cole-Parmer, Cat. No. A-27502-13) and conductivity meter (Jenco Electronics Ltd., Model 1671) calibrated using calibration standards (Cole Parmer, Cat. No. A-27502-63). The electrode was submerged into the flume immediately downstream from the cap.

5. CONCLUSIONS

We propose clay/cement composite as a new capping material for the isolation of contaminated sediments. By controlling post-depositional chemical processes in a forming composite it is possible to arrive at different cap microstructures leading to different mechanical and transport characteristics of the capping layer. Cement fraction and the extent of hydration of the composite appear to be the most important factors determining the overall performance of the cap.

ACKNOWLEDGEMENTS

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