Development of an active cap for the sequestration of mercury in contaminated lake sediments in Louisiana

Basic Information

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Project Number:	2010LA66B
Start Date:	3/1/2010
End Date:	2/28/2011
Funding Source:	104B
Congressional District:	Sixth
Research Category:	Engineering
Focus Category:	Sediments, Solute Transport, Treatment
Descriptors:	None
Principal Investigators:	K.T. Valsaraj, Ronald D. DeLaune

Publications

1. MRM Chaves, KT Valsaraj, RD DeLaune, RP Gambrell, PM Buchler, “Modification of Mackinawite with L-cysteine: Synthesis, characterization, and implications to mercury immobilization in sediment” Chapter in the book “Sediment Transport”, edited by Silvia Susana Ginsberg, ISBN 978-953-307-189-3, Intech Open Access Publisher, Vienna, Austria (2011).
2. M R M Chaves, K T Valsaraj, R D DeLaune, R P Gambrell, P M Buchler, “Mercury uptake by biogenic silica modified with L-Cysteine”, Environmental Technology (Accepted, In Press 2011)
3. MRM Chaves, KT Valsaraj, RD DeLaune, RP Gambrell, PM Buchler, “Mercury uptake by mackinawite modified with L-Cysteine”, Environmental Technology (Submitted, April 2011)
4. MRM Chaves, KT Valsaraj, JS Preston, RP Gambrell, RD DeLaune, PM Buchler, “Influence of L-methionine on the Mackinawite oxidation stability”, 2010 Goldschmidt Conference in Knoxville, Tennessee on June 17th, 2010

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Introduction

Mercury and its compounds are considered hazardous substances, due its bioaccumulation capacity and its toxics effects on human health. The main human exposure is through the aquatic food chain. Elevated mercury concentrations in fish are the leading cause of fish advisories. In 2008, 43% of the total lake acres in the United States were under advisory for mercury (USEPA, 2009).

The Louisiana Department of Environmental Quality (LDQE) has listed in the 2000 Annual Mercury Report nineteen areas under fish consumption advisory spread along of the State. The sediment of all these areas were contaminated, but only five areas have shown sediment with mercury concentration higher than 0.200 mg/kg.

The potential sources of mercury in Louisiana are numerous, including atmospheric deposition, natural geologic deposits, industrial/municipal discharges, and previous contaminated sediments (LDQE, 2001). The industrial and municipal discharges include chlor-alkali plants, hazardous waste, municipal waste incinerators, chemical manufacturing plants, and coal-fired utilities. The Louisiana State has twenty-six facilities included in the LDQE's Toxic Emission Data Inventory (TEDI). Three facilities have reported mercury release to the surface waters of Mississippi and Calcasieu Rivers. According with LDQE (2001), the total mercury released to the environment of Louisiana from 1991 until 1999 was about 8,281 kg.

The hydrologic system of Louisiana is composed by great number of rivers, bayous and lakes. Most drainage leaves the State through the Mississippi River or flows into Lake Pontchartrain or directly into the Gulf of Mexico through smaller streams. This characteristic it seems one reason for the high mercury contamination of Gulf of Mexico coastal area in Louisiana. Thus, the remediation of sediments from lakes and rivers is important not only for the rehabilitation of the local environment, but also for the mercury transport decrease to the areas of the Gulf of Mexico.

Effective remediation of sediment contaminated with mercury is essential to minimize the contamination of fish and shellfish and, consequently, the human exposure to methyl mercury. In situ capping (ISC) is one of the remediation methods that have been shown to be effective in reducing mercury transport from contaminated sediments (Liu, Valsaraj and Delaune, 2009). In-situ capping consists in placing a layer of proper isolating material between the layers of contaminated sediment and overlying water. This method is useful in reducing the transport of the contaminant, and requires less infrastructure associated with the handling, dewatering, treatment and disposal process.

Reible (2006) discussed the sediment remediation and related that sand has been used as cap material due it being readily available, relatively inexpensive and easy to place. Sand provides many of the basic protective features of a cap; however, alternative materials could be used to improve additional effectiveness of cap. Reible is leading a demonstration of effectiveness of some materials used as capping material in field condition, in the Anacostia River - Washington DC, including coke, apatite, and aquablock®. He advised the use of coke to organic contamination, and nano sized zero valent iron where there is polychlorinated organics contamination.

As an innovative approach, Reible et al (USEPA, 2009b) are evaluating bauxite as capping material to mercury sequestration in sediment. Also, he states that cost and placement concerns normally preclude the use of conventional broadcasting techniques for these materials.

Wang et al (2004) presented a literature review of the application of sediment-capping techniques. Most of the materials presented for capping purpose were based on sand and gravels layers.

Jacobs and Forstner (1998) proposed the idea of using active barrier systems (ABS) with in situ capping (ISC). ABS usually is a reactive geochemical barrier layer that can actively block the contaminant release from the sediment entering into the overlying water, without the hydraulic contact between the sediment and the overlying water being disturbed. They used natural and modified zeolites as active material. Despite they have used to lead sorption, this feature has improved the concept of mercury sequestration using in situ capping, once mercury does not have large chemical affinity by silicate-based materials commonly used in ISC.

Sulfur, as sulfide ion, is well known to have great chemical affinity with a wide number of divalent metal ions, especially mercury. Based in this characteristic and in the chemistry of iron sulfides, Liu, Valsaraj and Delaune (2009) used mackinawite (FeS) as ABS with capping to the mercury uptake and methylation inhibition on contaminated sediment.

Liu (2008) developed her PhD works about the mercury transport through capped sediment with mackinawite. Her results have shown that mackinawite present superior efficiency on mercury immobilization (1.25 g Hg/g FeS in mercury concentration solution of 3.5mMol/l), and inhibition of mercury methylation, than sand and zeolites. However, Liu advised about the lower oxidation resistance of this material, limiting factor to use in field conditions.

We proposed the modification of mackinawite with L-cysteine, due its antioxidant property. Previous results have shown that modified mackinawite is more stable to oxidation than the unmodified mackinawite. Also, it was observed that modification process do not influence the mercury sequestration capacity, being higher than the inorganic materials (490 mg Hg/g FeS-Cys, in 10 minutes of contact). However, the effect of the mackinawite modification on the mercury sequestration in sediment was not determined.

The aim of this project was to evaluate mercury sequestration in sediments of Henderson Lake, LA, using modified mackinawite. This evaluation comprised of the following:

a) To evaluate the mercury contamination level of sediments of a selected area;
b) To evaluate the capping technology using modified mackinawite to prevent and minimize the transport of mercury from contaminated sediment to water column of the selected areas;
c) To determine the efficiency of modified mackinawite to mercury sequestration in contaminated sediments, as an isolating material in capping.

The project comprised the determination of the mercury methylation inhibition capacity of modified mackinawite using contaminated sediment; and the evaluation of mackinawite as active material in in-situ capping. However, it was also was needed to evaluate the mackinawite synthesis and characterization, surface modification and, the evaluation of mercury sequestration by mackinawite from aqueous solution.

Background Research

Unmodified synthetic mackinawite has lower oxidation resistance, and it constitutes a limitation for its use, especially in capping technology. We have been working on mackinawite, in order to make this suitable to capping. We prepared pure mackinawite and mackinawite modified with L-cysteine, characterized the structure of the solids, evaluated the oxidation stability, and verified the mercury sequestration capacity in mercury spiked solution.

The following results constitute the background for the experiments of mercury sequestration from contaminated sediment in Louisiana, using in-situ capping technology.

Synthesis and characterization of modified and unmodified mackinawite

The chemical composition of unmodified mackinawite was determined as $FeS_{0.86}$, using elemental analysis (CHNS) and ICP-OES analysis to determine iron content. Sweeney and Kaplan (1973) also found that FeS has a composition of $FeS_{0.87-0.92}$. For modified mackinawite, the chemical composition was determined as $FeS_{0.735}.Cys_{0.0133}$. The results of the chemical composition characterization, supported by others analytical techniques, indicate that L-cysteine is not adsorbed on the surface of mackinawite but incorporated into the structure by replacing the sulfur. We observed by XRPD that the structure can remain stable, as mackinawite, even with a deficiency of 13% in mole of sulfur, compared to synthetic mackinawite obtained without cysteine. This feature results in layered nano-crystalline solid. XRPD and TEM analysis showed increase on (001) spacing, indicating that L-cysteine reacts with the iron, when mixed during the synthesis, and remains within the structure of mackinawite, between layers. The lattice expansion could facilitate the mercury sequestration process.

The L-cysteine affects the morphology of mackinawite clusters, being a result of its orientation and attachment during the synthesis. Cysteine takes place between the sheets of the FeS, and it forces the clusters to form plates. TEM results showed particles with average diameter of 5 nm for both modified and unmodified mackinawite. XPS and EDS analysis supported the chemical composition determination, showing the presence of Fe^{2+} and S^{2-} as the main species. Also, they indicated that modified mackinawite has higher oxidation stability than unmodified mackinawite, through the presence of oxidation products.

Oxidation resistance study of modified and unmodified mackinawite

Experiments to evaluate the oxidation resistance of modified and unmodified mackinawite were performed. This evaluation was based on Eh, pH and dissolved oxygen characteristics of experiments with suspensions under magnetic stirring in more than 600 rpm, opened to the environment. Results demonstrated that FeS-Cys is more stable than the FeS, in pH range 5 to 8. In pH 4, both solids rapidly oxidize.

The most important result of the mackinawite modification with L-cysteine (FeS-Cys) is that the solid is 55% more stable to oxidation, in the experimental conditions of pH 6, temperature of 25°C, flask open to air, and mackinawite concentration of 2 g/L.

The temperature affects the mackinawite oxidation. It was observed that an increase in temperature inhibits the oxidation process. The oxidation reaction is dependent on the dissolved

oxygen in water, which decreases at higher temperatures. Even though, the Eh pattern of modified mackinawite, during the oxidation experiment, was lower than to the unmodified mackinawite in 25°C and 35°C, indicating the higher oxidation stability of modified one. In temperature of 45°C all mackinawites showed the same pattern, due the critical concentration of dissolved oxygen have limited the oxidation process.

These results were very important, and indicated that the modified mackinawite might be applied as an active insulating material in in-situ capping.

Hg (II) sequestration by modified and unmodified mackinawite

Experiments to determine the mercury sequestration capacity of the modified mackinawite was carried out, using solution of $HgCl_2$ dissolved in high pure water. Results showed that L-cysteine does not affect the mercury uptake capacity or kinetics on modified mackinawite, being capable to uptake 99.94% of mercury in solution within 10 minutes of contact. It means approximately 490 mg Hg/g FeS in media concentration of 1mmol/l Hg (II).

The pH affects Hg (II) sorption at low aqueous Hg concentrations, but that effect decreases with at high pH values. Sorption curves for Hg (II) on modified mackinawite, as function of initial concentration of Hg (II) and mackinawite, showed the same pattern as that on unmodified mackinawite, indicating no sensible difference in mackinawite adsorption capacity. The results were confirmed by XRPD and XPS. Cinnabar and metacinnabar were observed as the main product of sorption present in both modified and unmodified mackinawite.

Thus, the results established that the modification of mackinawite with L-cysteine did not affect the mercury uptake capacity, and resulted in the same products as the unmodified mackinawite. This feature is significant, making the mackinawite modification with L-cysteine as one alternative to make possible its use associated with in-situ capping.

Influence of organic matter on the Hg (II) sequestration by mackinawite

The influence of organic matter on the mercury sequestration capacity of mackinawite was evaluated. To simulate the organic matter presence, three concentrations of humic acid (Aldrich regent) were added to solution of 1 mmol/L Hg (II). After dissolution, pH correction, and deoxygenating, each solution was put in contact with modified and unmodified mackinawite, to evaluate the mackinawite capacity of sequestration of mercury associated to organic matter. Results showed that the mercury sequestration capacity of mackinawite is strongly dependent of pH and humic acid concentration. The mercury uptake increased as pH increase in the range 3 to 5.6, then decreased until pH 8; this pattern is common for both mackinawites. This pH behavior is accentuated as higher the presence of humic acid. Considering the concentration of humic acid 1.5 g/L, and unmodified mackinawite, the mercury sequestration were about 59%, 7%, and 2%, when pH was 5.6, 7, and 8, respectively. For these pH values the Hg (II) sequestration were about 69%, 46%, and 9%, when used modified mackinawite. These results indicated that, in neutral pH and in presence of organic matter, the modified mackinawite is more efficient in Hg (II) sequestration than unmodified mackinawite.

Materials and methods

The study of sequestration of mercury in contaminated sediments from Louisiana was conducted in the laboratory in in-situ capping microcosms, using modified mackinawite as an

active material for mercury immobilization. For comparison, unmodified mackinawite was prepared and studied under the same conditions.

The sediment collection and characterization, the potential of mercury methylation inhibition through sediment incubation, and the evaluation of mercury sequestration by mackinawite as a capping reactive layer are described below:

Sediment collection and characterization

To realize this study, sediment was collected from Henderson Lake, and analyzed to determine the presence of mercury (total mercury, and methyl mercury). The surface sediment (0-150mm) was collected with a Van Veen grab sampler and placed in a 5 gallon HDPE bucked. A 5 cm layer of surface water was placed over the sediment in order to maintain anaerobic conditions. These buckets were sealed, shipped to the lab and stored in a refrigerator (4°C). Prior to use, the sediment was sieved by using a steel mesh with 11mm openings to remove large debris. The sediment moisture was determined by weight change upon drying at 110°C for overnight. Organic matter content was determined as weight loss on ignition (LOI) - under temperature of 550°C during overnight – of the dried sediment samples. The pH of collected sediment was represented by the pH of the sediment slurry prepared by mixing sediment with the overlying water in a 1:1 ratio (weight), measured using an Orion ROSS pH Electrode 8156BNUWP and pH/mV meter (Oakton, pH 510 series). Sulfate in the pore water and filtrates were determined by conversion to barium sulfate, and turbidity measurement of suspension, using a 2100AN HACH turbidimeter, under EPA method 9038 (USEPA, 1986).

The total mercury content in the pore water was determined using a technique based on U.S. EPA method 7471A (USEPA, 1994), by centrifugation followed by vacuum filtration with 0.45 μm Whatmann filters .The solution was oxidized with aqua-regia and potassium permanganate (5%). Then, mercury content was determined using cold vapor absorption spectrometry (CVAAS). The total mercury content in the sediment will be determined using CVAAS of samples after acid digestion.

Methyl mercury content in sediment was determined based on the method of Alli et al. (1994), and Cai et al. (1996). The gas chromatograph separation and atomic fluorescence spectroscopy detection system will be used for quantification of Me-Hg. The integrated GC-AFS system include a Hewlett-Packard model HP 6890 Series with a gas chromatograph coupled to a PSA Merlin detector via Pyrolysis oven.

Mercury methylation study through sediment incubation

Liu (2008) have studied the mercury methylation inhibition potential of unmodified mackinawite. Thus, these experiments followed the same methodology, in an attempt to compare the results. Sediment and surface water from the site was mixed to form a slurry with a dry solid to water ratio of 1:9 (weight) placed in a 250 ml glass flask. The water content determined before the experiments was used to calculate the additional amount of surface water needed to make the slurry. Before each incubation experiment, the sediment was mechanically homogenized on a roller for 8 hours. During the incubation, the flask was sealed with a rubber stopper that had inlet and outlet holes. Ultrahigh-purity N2 was purged through the flask in order to maintain anaerobic conditions, with flow rate about 1-2 bubbles per second in the gas trap. The outlet gas was connected to a sulfide trap filled with the anti-oxidation reagent (AOR) (Brouwer and Murphy, 1994). The incubation flask was wrapped with aluminum film to prevent

possible decomposition of MeHg which may be caused by exposure to light (Hammerschmidt and Fitzgerald, 2006). The experimental setup is shown in Fig. 1.

Nitrogen was purged for 30 minutes; then mackinawite (unmodified or modified) was added in one concentration of 0.05 mmol/(g-dw), 0.167 mmol/(g-dw) or 0.5 mmol/(g-dw). After 15 minutes, Hg (II) solution ($HgCl_2$ 1000 µg/ml standard solution - SCP Science) was spiked into the slurry for a final concentration of 2 µg/(g-dw). Experimental measurements showed that the pH of the sediment slurry decreased from 7.25 to 6.8 due to the addition of Hg (II) solution. The incubation process was about 14 days. At the end, the slurry was transferred to a HDPE flask, nitrogen was added to keep the anaerobic conditions; the flask was very tight closed and stored in the freezer until the analysis for mercury and methylmercury.

All the incubation experiments followed the same procedure except for the control experiments. The control was used to show how much MeHg was produced without addition of any potential inhibitors and thus show how effective the selected inhibitors inhibited Hg (II) methylation. For all the incubation experiments, two replicates were run simultaneously.

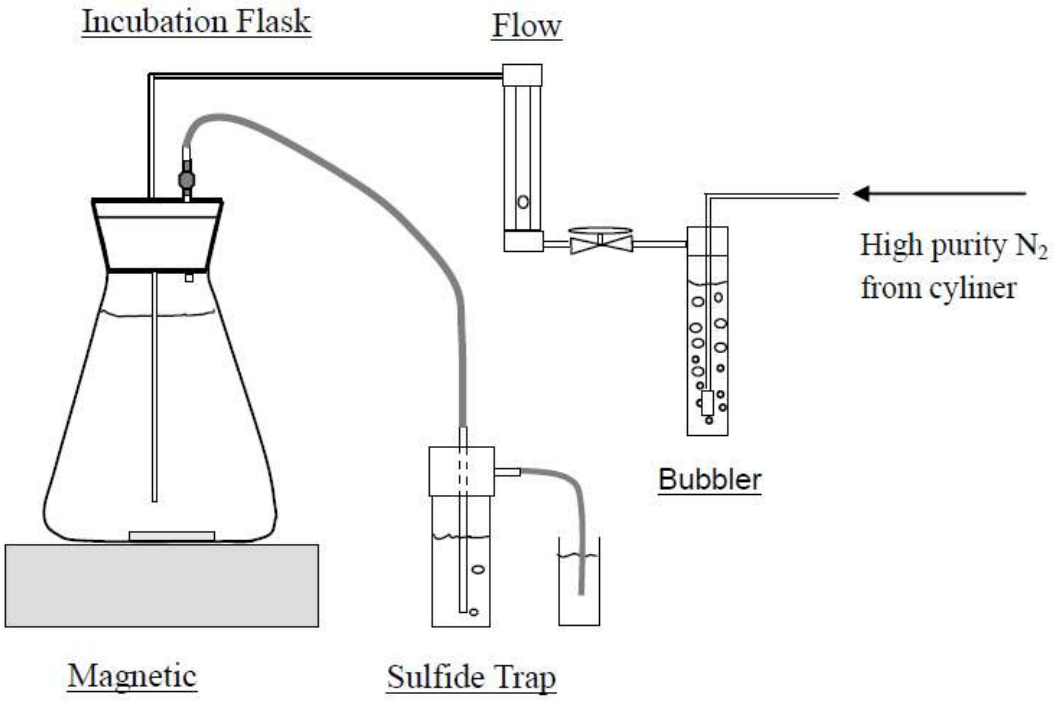


Fig. 1: Experimental setup for incubation experiments (Liu, 2008)

Capping technology evaluation, and determination of the efficiency of modified mackinawite for mercury sequestration in contaminated sediments

This evaluation has being carried through using acrylic capping simulator cells, to investigate the fate and transport of mercury in capped and uncapped sediments. Using the sediment collected in the area designed to this study, six cells were set up, one uncapped cell, and five capped cells with isolating material as described in the table 1.

The synthetic mackinawite (FeS) and mackinawite modified with L-cysteine (FeS-Cys) were prepared as described in Chaves et al (2011). The sand was purchase from hardware store, washed with tap water and detergent, rinsed with deionized water, and dried at 110°C before use. The sand used was the portion selected by two sieves with openings 0.125 and 0.85 mm in diameter. During the experiment, the cells were covered with aluminum foil (sides and top) to avoid direct exposure to light and avoid the potential algal growth. The top of the cells were covered with heavy metal plates to reduce possible evaporation of mercury to the air. Deionized water was passed over the sediment or cap during the experiment at a flow rate of 10 ml/hr for each cell. The depth of the overlaying water was about 12 mm. Teflon tubing was used at the outlet for water sample collection. The sediment was spiked with Hg (II) 40 µg/g-dw and homogenized during 8 hours in a roller. After this time, the sediment was transferred to the cells, and let to consolidate by 14 days.

Table 1: Design for the capping cells experiments.

Experiments	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	Cell 6
Cap layer	No	8 mm sand	8 mm FeS	8 mm FeS-Cys	3 mm Sand + 5 mm FeS	3 mm Sand + 5 mm FeS-Cys

The capping cell is illustrated in the figure 2. Its dimensions are 100 mm x 50 mm x 150 mm (L x W x H) for the part containing sediment, and 300 mm x 50 mm x 45 mm (L x W x H) for the part containing water. These cells were projected and used previously by Liu (2008), in her PhD works.

After the sediment consolidation, it was adjusted to the height with sediment, and covered with the desired capping material. Deionized water was passed over the sediment or cap during the experiment, and samples were collected to determination of mercury, and methyl mercury released to the overlying water.

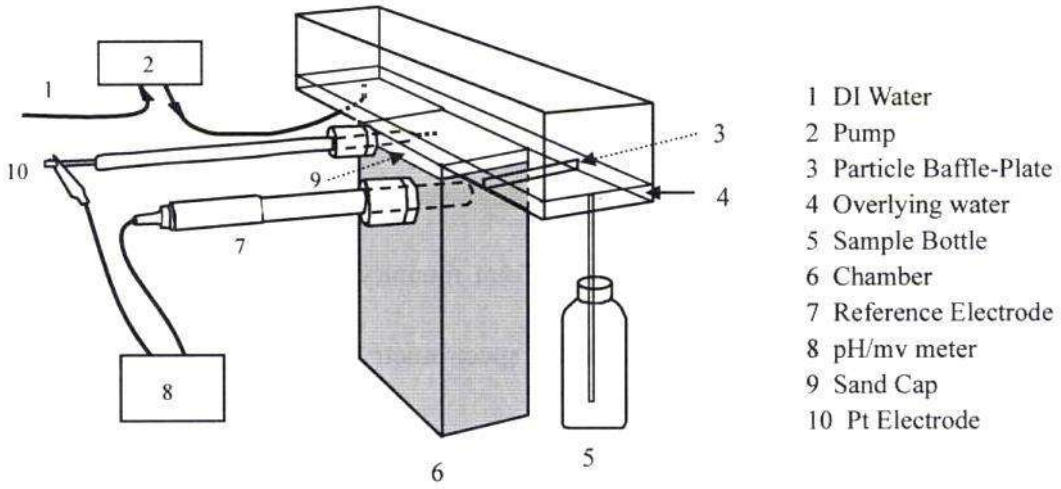


Fig. 2: Schematic of the capping cell (Liu, 2008).

The cells have being monitored to evaluate the redox conditions, and dissolved oxygen in the simulation system. The redox potential has being determined using reference electrode (Accumet, Fisher Sci.) and platinum electrodes. The platinum electrodes were made, cleaned and tested according Patrick et al (1996).

The platinum electrodes were tested in pH 4 and pH 7 buffer solutions of quinhydrone (Alfa Aesar). The reference electrode was installed 30 mm below the water-sediment/cap interface for each cell. For uncapped cells, the platinum electrodes were installed at 30, 20, and 10 mm below the water-sediment interface. For capped cells, of 5 platinum electrodes applied, 2 were in the cap layer (at 2mm and 5 mm from water-cap interface), 1 was at the cap-sediment interface (at 10 mm from water-cap interface), and the other 2 were in the sediment (at 30 mm and 20 mm from water-cap interface). The redox potentials were measured using a pH/mV meter (Oakton, pH 510 series). At the end of the experiment, the electrodes used will be tested again to verify if they were working in the acceptable range.

The dissolved oxygen in the cell 1 and 2 was measured with a Clark-style oxygen microelectrode coupled to a 1201 chemical microsensor (Diamond General Inc.). For the cells with mackinawite, it was observed that the Clark-style oxygen microelectrode was not proper to determine DO; it was determined using a Mettler Toledo InLab® 605 sensor, with internal ATC probe, connected to Mettler Toledo SevenGo™ Pro SG6 DO meter, which was calibrated following the manual instructions, using oxygen-saturated water.

The experiments were conducted over 6 months of operation. The sediments into the cells were then sliced and analyzed to determine the mercury migration on the system. The content of total mercury was determined using CVVAS, and methyl mercury will be determined using CG-AFS of digested samples for each depth. The results will allow building the profile of the mercury migration in the sediments, consequently, the fate and transport of mercury in these systems. The efficiency of FeS-Cys as an isolating material for capping will be determined by content of mercury and methyl mercury, present in sediment and water of all cells. The redox conditions, oxygen and mercury profiles, as well the sediments characteristics, will support this evaluation.

Results and Discussion

Two main problems occurred during the performance of this project, and they caused delays in the project. The first one was caused by the long time required to synthesize the modified and unmodified mackinawite in large quantity. The procedure of synthesis in laboratory scale required at least 3 days (for synthesis and purification) to produce about 2.5 grams. Overall, we needed 3 months to prepare 120g of each mackinawite, resulting in delay of 6 months to the experiment start up. The second problem was that the equipment to analyze methyl mercury was under repair during August to December 2010, and no sample could be analyzed. The start up of the capping experiments was in September 2010, and it cored in April 2011. Thus, the experiments are yet to be finalized, the samples analyzed, and the results presented.

Mercury sequestration in contaminated sediments: The efficiency of modified mackinawite, as an isolating material in capping.

The efficiency of modified mackinawite as an isolating material in capping will be determined through the measurement of the total mercury released from sediment to overlying water, as well the methylmercury and total mercury profile in the sediment and cap layer. All the analysis for total mercury and methylmercury will be performed after the end of the experiment, and the results will be presented in the final report.

Mercury methylation study through sediment incubation.

The potential of mercury methylation inhibition of the modified mackinawite was performed through the sediment incubation. The samples were preserved frozen, and will be analyzed for methylmercury and total mercury; the results will be presented in the final report.

Evaluation of the mercury contamination level in the sediment.

The sediment collected from Henderson Lake was analyzed, regarding sulfate, AVS, pH, presence of organic matter, total mercury, and solid content. The results are summarized in table 2. It was observed that the sediment sample was in the neutral range (pore water and surface water).

The sulfate in surface water was in higher than the results reported by Liu (2008). The sulfate concentrations are higher in the winter and lower in the summer and fall (Suplee and Cotner, 2002); it can explain the observed high level of sulfate in the pore water, since the sediments were collected in March 2010, winter in Louisiana.

The AVS and total mercury concentration was lower than those observed by Liu (2008) for sediment from Henderson Lake. The sediments did not exceed the limit of 200 ng/g-dw, and showed close to the median mercury concentration (40 ng/g-dw) in sediments of Louisiana State (USEPA, 1997).

Table 2: Summary of the sediment characterization results.

Solid (%)	**Sulfate in sediment (µmol/g-dw)**	**Sulfate in surface water (µmol/L)**	**pH surface water**	**AVS (µmol/g-dw)**
53.3	7.53±0.48	899±4.5	7.6	6.72±0.25
Organic matter (%)	**THg sediment (ng/g-dw)**	**MeHg sediment (ng/g-dw)**	**pH pore water**	
2,8	45±3,6	To be determined	6.9	

Evaluation of the capping technology using modified mackinawite.

The capping technology evaluation using mackinawite as reactive medium has being performed through acrylic simulator cells. It was observed during the cells preparation that a minimum disturbance is enough to disperse mackinawite into the water column; once dispersed in water, is hard to mackinawite decant, due its very small size of the clusters. Thus, is not recommended to spread mackinawite in the water column, but it can be applied, for example, by slurry pumping.

The mackinawite oxidation is an important parameter to be considered, once after sorption, this process might remobilize mercury, resulting in many problems associated to its availability. The DO, pH, Eh and sulfate releasing are the parameters to monitoring the oxidation process of the species in the sediment and mackinawite cap layer, into the cells

Dissolved oxygen in the cells

The cells design allowed the top part, the water column, to be in contact with air, once the cells were not hermetically closed. This feature plus the feeding water kept the water column and water/sediment-cap surface with aerobic conditions. Considering the water/sediment (or water-cap) surface as zero level, the sediment of both cells uncapped and capped with sand were anoxic in 10 mm of depth. The dissolved oxygen (DO) concentration changed as shown in the figure 3. For the sand capped cell, the DO level was higher than uncapped one, due the cap porosity allowing the oxygen diffusion.

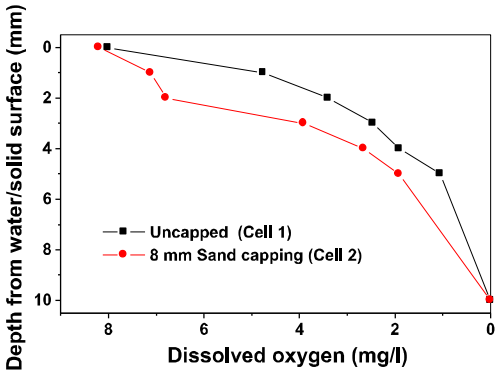


Fig. 3: The DO profile of Cells 1 and 2 after 7 days of the experiment start up.

Mackinawite in contact with water produces a fast consume of DO, resulting in strongly anoxic medium. This behavior was confirmed for the cells 3 to 6, in which the DO at zero level was 0.02 mg/L, 0.03 mg/L, 1.31 mg/L, and 1.47 mg/L for cells 3, 4, 5 and 6, respectively. After 71 days, the DO level was unchanged for cells 3 and 4; for cells 5 and 6, the DO level increased for 4,07 mg/L and 3, 67 mg/L, respectively, due the sand cap upon the mackinawite layer allow the oxygen diffusion.

pH and sulfate released during the capping experiments

Mercury sorption and desorption as well mercury methylation process in sediment depend on the specific characteristics of the sediment and mercury speciation; both are directly related to the pH of the medium. Low pH is related to high mercury methylation process, as a result of several factors such as increasing in mercury desorption (Liu 2008). The pH is also important parameter to describe the reactions which take place on the sediment and water/sediment surface.

The pH of the effluent of uncapped cells, and cells capped with sand was close to the pH of the anoxic sediment after mercury amendment, around 7. It did not change during the experiment, due the absence of intense chemical reactions on the sediments.

Mackinawite is very reactive and easily oxidizes when expose to the oxygen. In the cells it occurs in the aerobic zone, above 10 mm in depth of the water/sediment surface. The oxidation process produces [H^+]; thus, the lower pH, the higher the mackinawite oxidation. The capping layer of 8 mm in the cells 3 and 4, and 5 mm in the cells 5 and 6, had a high quantity of iron sulfide. Therefore, the oxidation process was intense enough to produce sensible pH decreasing, more than the oxidation of the sediment in direct contact with the column water (cell 1).

The pH of the effluent of the cells using unmodified mackinawite decreased below 7 in less time than the cells using modified mackinawite, confirming that the mackinawite modification with L-cysteine improves its oxidation resistance.

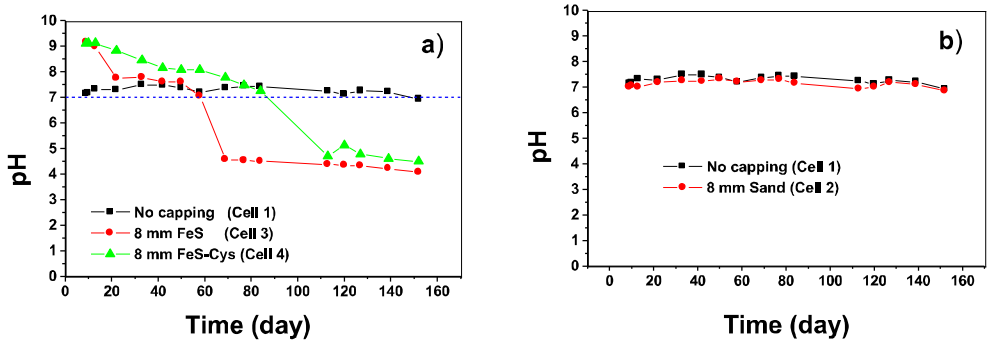


Fig 4: pH of cells uncapped and capped with sand layer.

The pH of the water effluent from cells capped with mackinawite, with and without sand layer, followed the characteristics of the used mackinawite (Fig. 5). Considering the cell 2, the 3mm sand layer is enough to reduce the DO of 8 mg/l to 4 mg/l. Thus, a sand layer reduces the DO in the cells 5 and 6, consequently, the mackinawite oxidation, making this process less intense in comparison to the cells 3 and 4. For cell 6 (Fig. 5b), the pH of the effluent was around 7 during the experiment, indicating that modified mackinawite combined with a sand layer is a good capping layer design to inhibit the mackinawite oxidation.

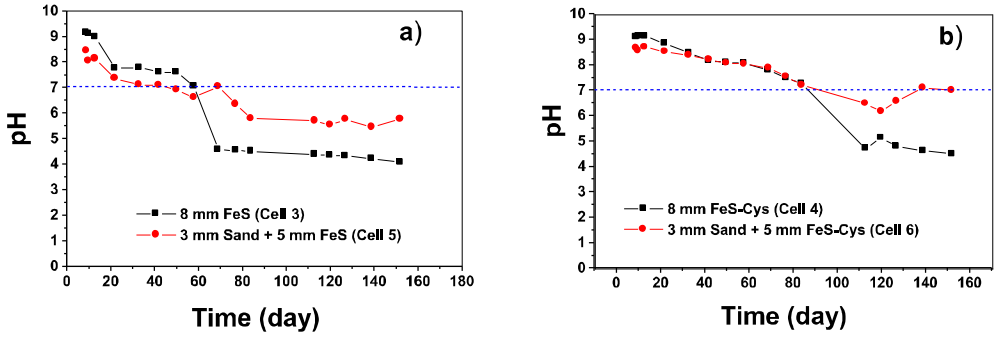


Fig. 5: pH of cells containing mackinawite during capping evaluation.

The iron sulfide (as mackinawite) is the main constituent of acid volatile sulfide (AVS) present in anoxic sediment. The mackinawite oxidation mechanism involves the oxidation of sulfide to polysulfide groups, passing through the elemental sulfur and then to sulfate (equation 1 and 2). The sulfate ions released to effluent water is related to the pH in the opposite profile.

$$FeS + \frac{1}{2}O_2 + \frac{3}{4}H_2O \rightarrow FeOOH + S^0 \quad (1)$$

$$S^0 + \frac{3}{2}O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (2)$$

The pH was almost constant in the cells 1 and 2 (Fig 6a, and b); consequently, the sulfate released followed the same trend. The sulfate released from the uncapped cell (cell 1) was about 70 mg/L at the experiment start up, and decreased below 40 mg/L during the experiment. Some drift occurred, but the sulfate releasing was below of the 70 mg/L over the time. The same was observed to the cell 2, capped with 8 mm of sand, where the sulfate released was below 100 mg/L; the higher sulfate releasing than the cell 1 is attributed to some sulfate adsorbed during the sand cleaning procedure with detergent.

The cells with mackinawite did not showed an aerobic zone, once all oxygen that diffuses from air to water column was continually consumed by mackinawite during its oxidation process. The sulfate released from cells 3 and 4 showed the same trend, but the quantity was lower for cell 4, due the higher oxidation resistance of modified mackinawite. During the initial 60 days, sulfate was released in very low concentration, corresponding to the oxidation inhibition phase. After them, the sulfate release has increased, due the fast oxidation of mackinawite (Fig 7c). The sulfate released from cells 5 and 6 was lower than the cells 3 and 4, confirming that the additional sand layer prevent the oxidation of mackinawite (Fig 7d).

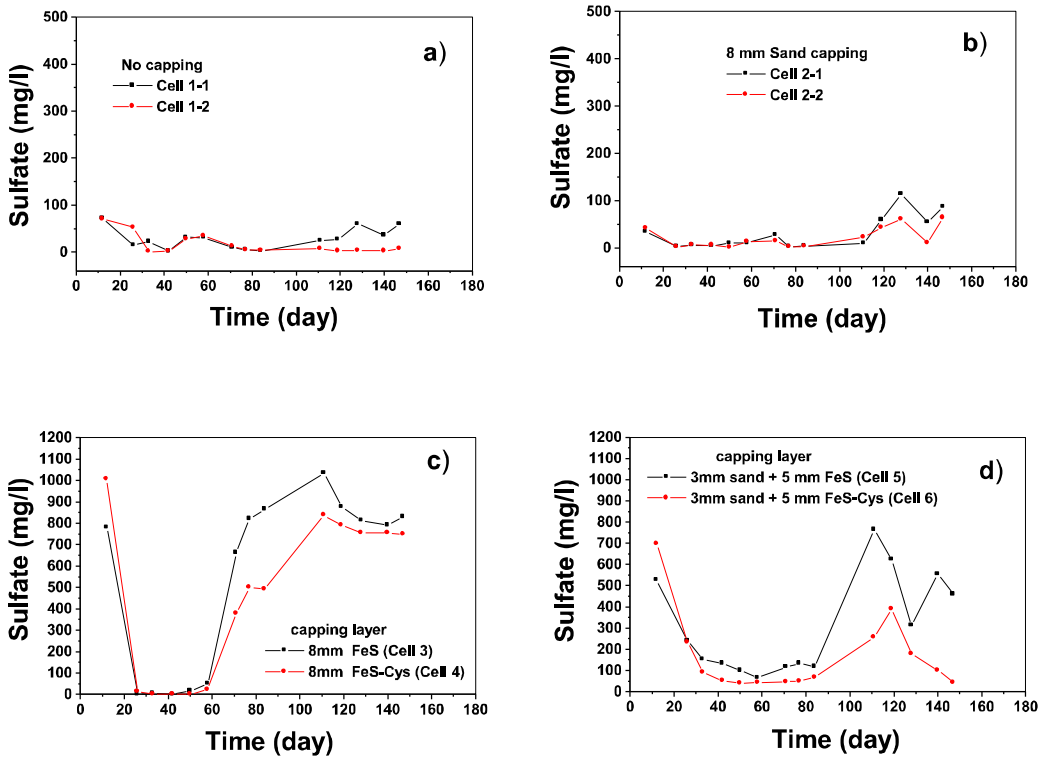


Fig. 7: Sulfate released from cells during the experiment.

Despite the experiment was not finished, the amount of sulfate released into the water until the last measurement was determined from equation 3 (Liu 2008).

$$n = \sum_i Q * C_i * \Delta t_i \quad (3)$$

Where:

n: Total sulfate released to the water;

Q: The flow rate of water (10 ml/h);

i: ith sample collected;

C_i: Sulfate concentration in effluent water of sample I;

Δt_i: Time interval between sample i and sample (i-1) were collected.

The total sulfate released from cells 1 to 6, during 147 days, is presented in the figure 8. It was observed that the modified mackinawite released about 17% (mol) less sulfate than the unmodified one. Considering the cell with unmodified mackinawite (cell 3), the sulfate released decreased about 42% when a sand layer was used (cell 5). Similarly for cell with modified mackinawite (cell 4), occurred a decreased about 62% for cell 6, and this percentage represents the contribution of the sand layer and the L-cysteine modification effect over the mackinawite oxidation in the cells.

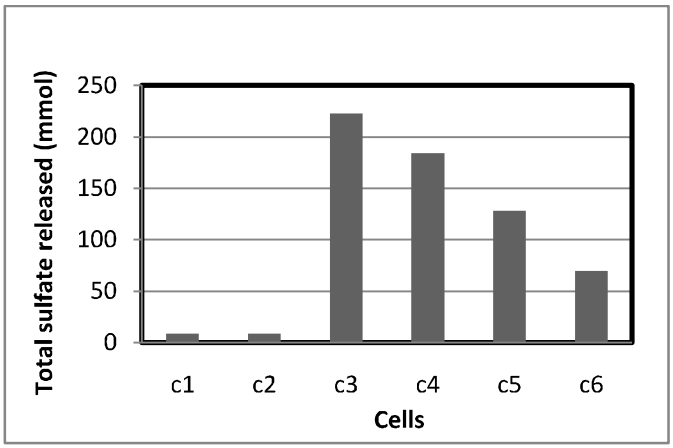


Fig. 8: Total sulfate released from cells during 147 days.

Redox conditions of cells

The uncapped sediment showed the Eh typical profile for anoxic sediments (Fig. 9a). At beginning of the experiments, the Eh drifted due the electrodes stabilization process. During the experiment, the top of the sediment was oxidized, resulting in slightly increasing in Eh of the sensor at 10 mm.

The cell capped with 8 mm of sand showed the Eh profile with characteristic parts across the cells (Fig. 9b). The top part, above 2mm, the cap conditions was aerobic; therefore,

the Eh is very positive. It can be observed that the Eh of the sensors at 0 mm and 2 mm present an abrupt change after 80 days of the experiment. It was attributed to the sediment motion upward, probably due the detachment of gas bubbles from the sediment. This movement took the anoxic sediment with lower Eh to the top, exactly where the electrodes were placed, resulting in decreasing of the Eh read (Fig. 10). At the bottom part, below 10 mm of depth, the sediment was anoxic, and the Eh was similar to of same depth of the uncapped cell.

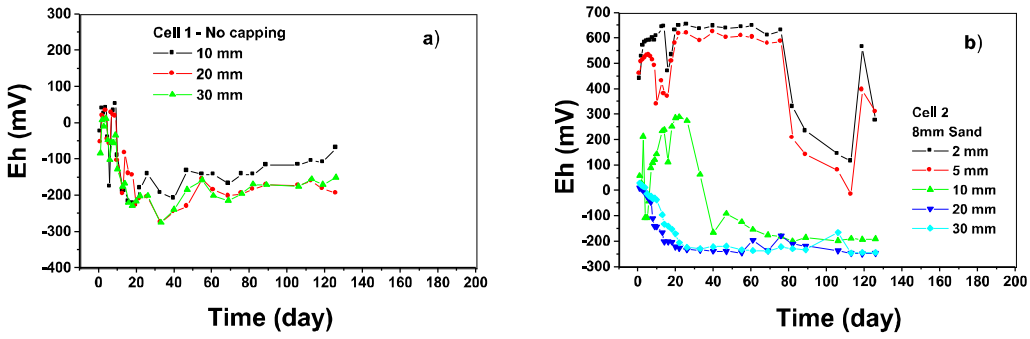
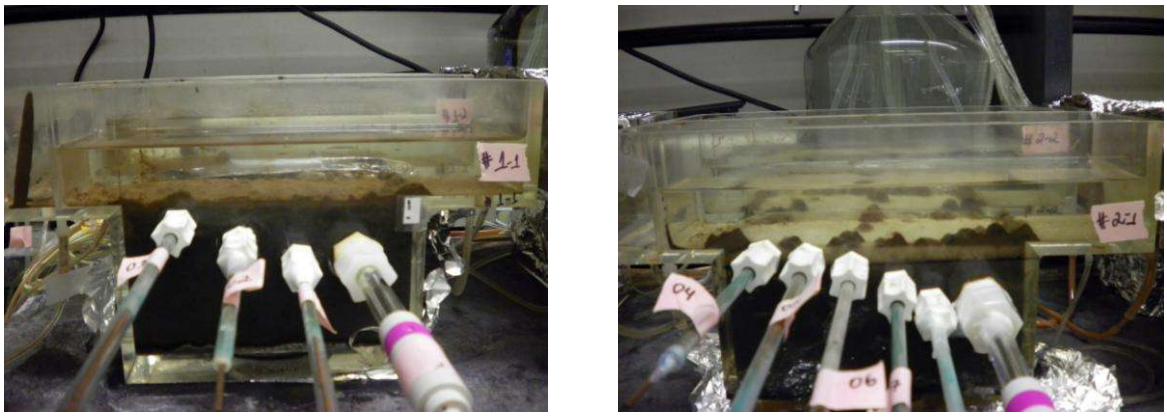


Fig. 9: The Eh in the cells 1 and 2 during the experiment.



a) b)

Fig. 10: The capping experiment after 60 days: a) cell 1; b) cell 2.

The potential redox in the cells capped with synthetic mackinawite describes the oxidation process of this material studied in previous works (Chaves et al, 2011). The anoxic condition of the sediment and the water/sediment surface is attributed to the oxygen consume by mackinawite.

The modified mackinawite is more reductive than unmodified mackinawite, resulting in lower Eh showed by the sensors at 10 mm and 20 mm of depth (Fig. 11b). The sensor at 30 mm showed the Eh typical of this depth for the uncapped cell. During the experiment, it was observed an increasing in the Eh of sensors at 2 mm and 5 mm of depth, due the oxidation process. The top layer partially oxidized prevents the oxidation of the bottom part, as seen for the region of the sensors at 10 mm, 20 mm and 30 mm. For the cell capped with unmodified

mackinawite, the sensors indicate that the oxidation process occurs throughout the material (Fig. 11a).

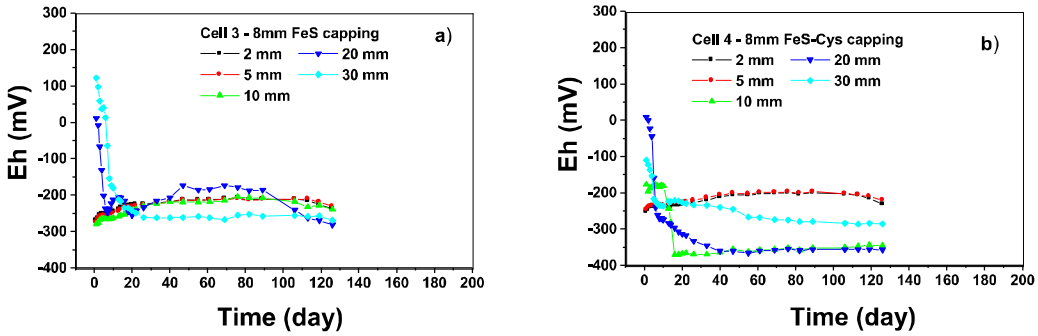


Fig. 11: Eh in the cells 3 and 4 during the experiment.

The cells with double cap layer (sand + mackinawite) showed the potential redox profile very similar than the cells with only cap layer of mackinawite for 10 mm of depth and below (Fig. 12). The top part was constituted of sand layer; the Eh is high, but not positive as cell 2, because mackinawite is very reductive, and acts surrounding areas, decreasing the Eh in the sand layer. Also, mackinawite is nano sized material and particles must have spread to the porous cap layer of sand, especially because this cell was disturbed during the start up process. This was visible in the cell 5, in which the sand layer and the water column turned black in color (Fig. 13).

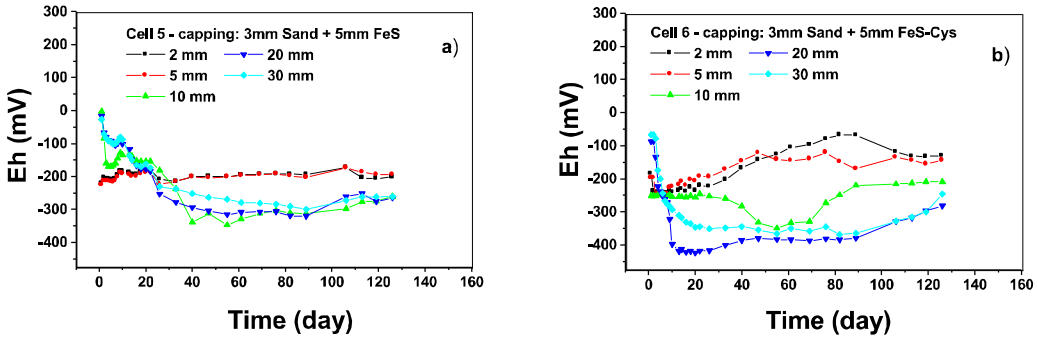
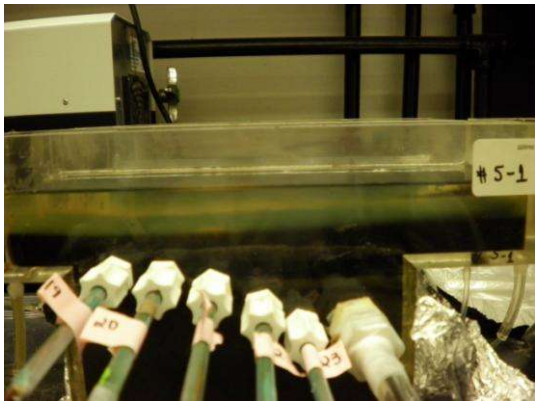
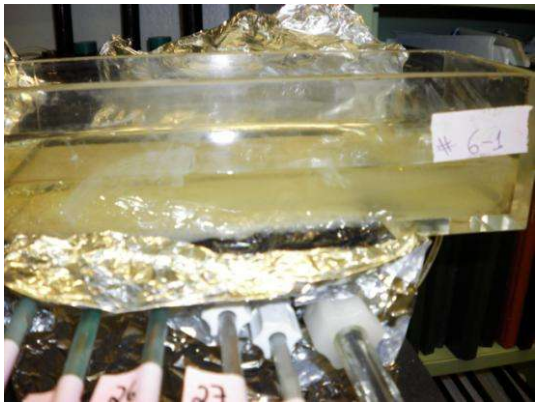


Fig. 12: The Eh in the cells 5 and 6 during the experiment.



a)



b)

Fig. 13: The capping experiment after 60 days: a) cell 5; b) cell 6.

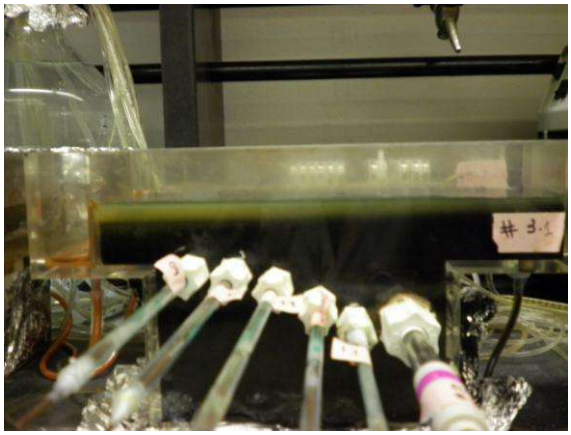
The oxidation resistance of modified mackinawite

The oxidation process of mackinawite in presence of oxygen presents two main phases: first occur the oxidation of the sulfide groups at the mackinawite surface, with the formation of polysulfide chains; it limits the oxygen diffusion to the bulk of the solid, working as a passivation layer. With the growth of these chains, it becomes more permeable to the oxygen diffusion, and a fast oxidation phase takes place.

Thus, to evaluate the oxidation resistance, we considered the time required to begun the fast oxidation phase. The oxidation resistance was associated to the capacity of passivation layer in prevent the oxidation of the bulk material.

Previous results showed that modified mackinawite is more resistant to oxidation than unmodified mackinawite (Chaves et al, 2011). It has being verified in the capping experiments by comparison of the results of pH, sulfate released, Eh profile in the cell, and visual inspection.

The figure 14 shows the cells 3 and 4 after 60 days of experiment. It can be observed in the cell 3 a yellowish layer of oxidized material in suspension at the top of the water column; it did not occur in the cell 4.



a)

b)

Fig. 14: The capping experiment after 60 days: a) cell 3; and b) cell 4.

Non oxidized mackinawite is black powder, which generates black dispersion. As it becomes oxidized, the black color turn progressively to red-brown, characteristic of iron (oxide) hydroxide; the degree of oxidation is related to the intensity of this color. The surface water of cell 3 showed a red-brown color, characteristic of advanced oxidation (Fig. 15). The higher oxidation resistance of modified mackinawite can be observed through the darker color of surface water that flowed from the cell 4.

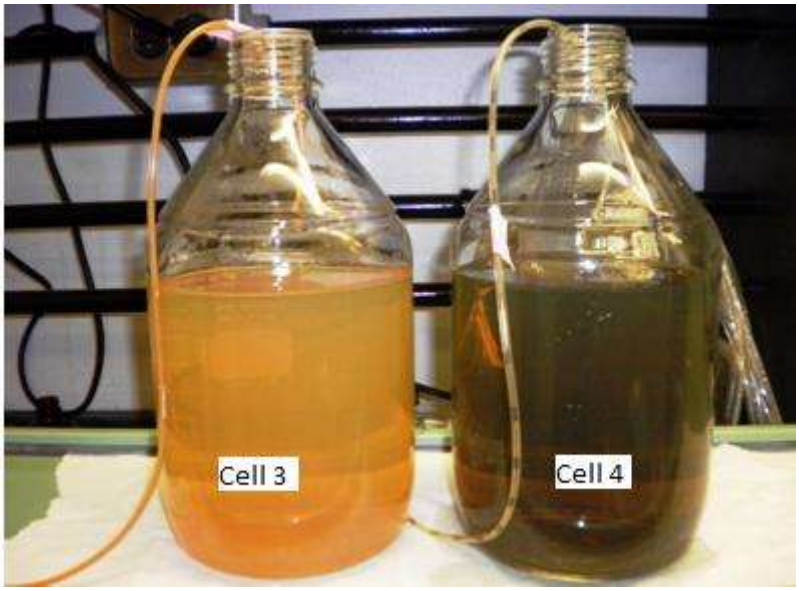


Figure 15: The surface water from cell 3 and 4 after 60 days.

After 80 days, the cell 4 showed a whitish layer at the top of water column, indicating that the intense oxidation process had begun. In comparison, the same layer in the cell 3 was ochre in color (Fig. 16), corresponding to the more oxidized material.

This event can be better verified by the pH results. It was observed that the pH of cell 3 decreased below 7 about 57 days of the experiment, and it occurred for the cell 4 about 85 days. It characterizes an increase on the oxidation resistance of modified mackinawite in 50% comparing with unmodified mackinawite; it confirms the value of 55% of oxidation resistance increasing described by the previous works (Chaves et al, 2011).

Figure 16: The capping experiment after 80 days for cell 3 and 4.

Conclusion

Preliminary results showed that the mackinawite modification with L-cysteine improves its oxidation resistance, when applied in capping cell simulators; it is very important and should allow the use of mackinawite as active material in in-situ capping technology. However, the particle size at nano scale was detected as a limitation, if applied as a powder. This will necessitate the development of a new methodology to build the capping layer under field conditions. The microcosm with modified mackinawite in a sand layer was the best design for in-situ capping experiment. It indicates that this microcosm should be useful in evaluating the mercury transport and mercury methylation through the sediment cap.

Peer-Reviewed Publications and Presentations Resulting from the Project:

One book chapter, three publications and one presentation have resulted from this work:

MRM Chaves, KT Valsaraj, RD DeLaune, RP Gambrell, PM Buchler, "Modification of Mackinawite with L-cysteine: Synthesis, characterization, and implications to mercury immobilization in sediment" Chapter in the book "Sediment Transport", edited by Silvia Susana Ginsberg, ISBN 978-953-307-189-3, Intech Open Access Publisher, Vienna, Austria (2011).

M R M Chaves, K T Valsaraj, R D DeLaune, R P Gambrell, P M Buchler, "Mercury uptake by biogenic silica modified with L-Cysteine", *Environmental Technology* (Accepted, In Press 2011).

MRM Chaves, KT Valsaraj, RD DeLaune, RP Gambrell, PM Buchler, "Mercury uptake by mackinawite modified with L-Cysteine", *Environmental Technology* (Submitted, April 2011)

MRM Chaves, KT Valsaraj, JS Preston, RP Gambrell, RD DeLaune, PM Buchler, "Influence of L-methionine on the Mackinawite oxidation stability", 2010 Goldschmidt Conference in Knoxville, Tennessee on June 17th, 2010.

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Chaves, M. R. M. et al (2011), *Modification of Mackinawite with L-Cysteine: Synthesis, Characterization, and Implications to Mercury Immobilization in Sediment*, Chapter in "Sediment Transport", ISBN 978-953-7619-X-X (in press), InTech Open Publishers, Vienne, Austria.

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