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Adsorption of Dissolved Metals in the Berkeley Pit using Thiol-SAMMS

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ABSTRACT

The Berkeley Pit in Butte, Montana, is heavily contaminated with dissolved metals. Adsorption and extraction of these metals can be accomplished through the use of a selective adsorbent. For this research, the adsorbent used was Thiol-functionalized Self-Assembled Monolayers on Mesoporous Supports (Thiol-SAMMS), which was developed at Pacific Northwest National Laboratory (PNNL). Thiol-SAMMS selectively binds to numerous types of dissolved metals. The objective of this research was to evaluate the loading and kinetics of aluminum, beryllium, copper, and zinc on Thiol-SAMMS.

Loading tests were conducted over a series of Berkeley Pit water to Thiol-SAMMS ratios (mL:g) of 5000:1, 1000:1, 500:1, 100:1, and 50:1. Kinetics tests were conducted at the Berkeley Pit water to Thiol-SAMMS ratio of 2000:1. The water from the Berkeley Pit was tested from the surface and from a depth of 750 feet. The pH of Berkeley Pit water is approximately 2.5; this is lower than the chemical stability range of Thiol-SAMMS (pH 4 – 10). Therefore, two parallel sets of loading and kinetics tests were conducted: 1) Berkeley Pit water, untreated, was tested with Thiol-SAMMS, followed by neutralization of the samples, and 2) Berkeley Pit water was neutralized to a pH of approximately 7 prior to addition of Thiol-SAMMS. Aqueous samples were analyzed using inductively coupled plasma – optical emission spectrometry (ICP-OES) and ICP-mass spectrometry (ICP-MS).

The results of the loading tests indicate that metal loading on Thiol-SAMMS decreased proportionally with the decreasing Berkeley Pit water to Thiol-SAMMS ratio in post-neutralized Berkeley Pit water. However, for solutions neutralized before addition of Thiol-SAMMS, the neutralization step resulted in precipitation of the majority of the dissolved metals before addition of Thiol-SAMMS.

The results of the kinetics tests showed that no change in the concentrations of the four metals was observed in the unneutralized Berkeley Pit water. This is likely the result of competitive adsorption between thiol hydrogen atoms and the dissolved metals. Under acidic conditions, the dissolved metal ions cannot exchange the thiol hydrogen atoms on the active sorption site (the binding site). Therefore, loadings observed in the post-neutralized loading test were likely due to neutralization and not metal loading on Thiol-SAMMS. Kinetic results from the pre-neutralized Berkeley Pit water were confounded by the precipitation of the aqueous metal ions prior to Thiol-SAMMS testing.

This study suggests that a significant decrease in dissolved metal concentration at Berkeley Pit could be realized through neutralization. Enhanced remediation techniques such as Thiol-SAMMS technology have a limited application under the highly acidic conditions posed by Berkeley Pit; however, Thiol-SAMMS could provide a secondary remedial technique which would complete the remedial system and remove dissolved metals from the Berkeley Pit to below drinking water standards.

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1. INTRODUCTION

Safe and healthy water supplies are a serious global issue. Fresh water supplies can become contaminated by many different types of chemicals originating from industrial and agricultural processes. The Berkeley Pit in Butte, Montana, is a former open pit mine that today contains over 40 billion gallons of contaminated water as a result of years of surface water and groundwater runoff into the pit (PitWatch 2009). Many different remediation techniques exist for decontaminating aquatic environments. Remediation technologies are usually specific for each type of chemical, such as organics and heavy metals. In this research the adsorption of aluminum, beryllium, copper, and zinc was tested by using Thiol-functionalized Self-Assembled Monolayers on Mesoporous Supports (Thiol-SAMMS), a selective adsorbent developed at Pacific Northwest National Laboratory (PNNL).

The United States Environmental Protection Agency (EPA) sets National Primary and Secondary Drinking Water Regulations (NPDWRs and NSDWRs, respectively) for different contaminants in drinking water. Primary regulations are enforceable and are set for contaminants that can pose health hazards, whereas secondary regulations are non-enforceable but recommended because of aesthetic issues in drinking water. Regulations are set in the form of maximum contaminant levels (MCLs). Beryllium and copper are both regulated by primary regulations. Beryllium has a MCL of 0.004 mg/L, and copper has a MCL of 1.3 mg/L. Aluminum and zinc are both regulated by secondary regulations. Aluminum has a MCL range of 0.05 to 0.2 mg/L, and zinc has a MCL of 5 mg/L (EPA 2009).

The United States Agency for Toxic Substances and Disease Registry (ATSDR) and the EPA have information on the environmental and health effects of aluminum, beryllium, copper, and zinc, as well as many other toxic substances. Beryllium can be harmful if inhaled or ingested. It can potentially cause acute beryllium disease and, more seriously, chronic beryllium disease (CBD) can form in people sensitive to beryllium (ATSDR 2002). Aluminum is also potentially harmful to human health. People who are exposed to aluminum in high levels may develop Alzheimer's disease. Although some studies support this finding, there are others that do not. In addition, some people with kidney disease have a high concentration of aluminum in their bodies. Some have developed bone or brain diseases that may have been caused by an excess of aluminum (ATSDR 2008). In addition, copper and zinc are both necessary for life but can be harmful at high concentrations (EPA 2006 and ATSDR 2005).

The Berkeley Pit in Butte, Montana, was an open pit mine operated from 1955 to 1982. Groundwater inflow and surface water runoff were continually pumped out of the mine during the 27 years of operation. Once the pit closed, the pumps were shut off and water began filling the mine shafts and the pit (Dysinger 1998). Today, the pit holds over 40 billion gallons of water, and the water level is approximately 5,280 feet above sea level (PitWatch 2009). The Berkeley Pit surface water has a pH of about 2.5 through a depth of approximately 750 feet. The EPA and the Montana Department of Health and Environmental Sciences set a maximum critical water level (CWL) for the Berkeley Pit

of 5,410 feet above mean sea level (ft msl), at which point the pit will have approximately 64 billion gallons of water. The CWL was set to prevent Berkeley Pit water from entering the alluvial aquifer or Silver Bow Creek drainage (EPA 1994). The 1994 EPA Record of Decision for Silver Bow Creek/Butte Area estimates that if no remedial efforts are carried out in the Berkeley Pit, the CWL will be approached by 2015 (EPA 1994). A photograph of the Berkeley Pit, taken by a NASA astronaut in space on August 2nd, 2006, is shown in Figure 1.



Figure 1. The Berkeley Pit as seen from space, photo taken on August 2nd, 2006 (NASA, 2008).

Many different methods exist for removing dissolved metals from water. Some of the more common methods are ion-exchange, membrane processes, and adsorption. Ion-exchange is a reaction between ions in a liquid phase and ions in a solid phase. In this reaction, ions from the liquid solution are exchanged with different ions from the solid solution (Reynolds and Richards 1996). Membranes allow exchange of ions between two solutions. Selectively permeable membranes may be made out of different materials such as zeolite (Zou et al. 2009). Selectively permeable membranes allow only certain ions to pass between the solutions. The focus of this research is on adsorption. In adsorption, an adsorbent binds to ions in solution. An adsorbent usually has a high surface area to mass ratio to allow more binding sites on the adsorbent.

Thiol-SAMMS is the adsorbent used in this research. Thiol-SAMMS has a thiol functional group, which is a hydrogen bonded to a sulfur (HS). Metals bind to the sulfur in this group and remove the bound thiol hydrogen. Thiol-SAMMS has a high surface

area to mass ratio (approximately 1000 m²/g). It selectively adsorbs certain metals, such as mercury, copper, and silver. It adsorbs minimal amounts of alkali and alkali earth metals such as sodium, magnesium, and calcium (PNNL 2008). For certain metals, Thiol-SAMMS has a large loading capacity, meaning that a relatively large amount of metal ions can adsorb onto a small amount of Thiol-SAMMS. Moreover, because of these qualities, Thiol-SAMMS is a good choice of adsorbent to test in Berkeley Pit water.

To prevent contamination of the aquifers in the area, immediate remediation efforts in the Berkeley Pit are necessary before the water level reaches the critical water level. The research presented here shows the results of adsorption tests using Thiol-SAMMS adsorbent on Berkeley Pit water.

2. EXECUTIVE SUMMARY

This research has been supported by the DOE-FIU Science and Technology Workforce Development Initiative Program. During the summer of 2009, a Florida International University (FIU) DOE Fellow (Amaury Betancourt) spent 10 weeks performing a summer internship at Pacific Northwest National Laboratory (PNNL), under the supervision and guidance of Dr. Dawn Wellman. The objective of this research was to test how well the adsorbent Thiol-SAMMS (Thiol-functionalized Self-Assembled Monolayers on Mesoporous Supports) can adsorb dissolved metals, specifically aluminum, beryllium, copper, and zinc, from the contaminated water of the Berkeley Pit in Butte, Montana. The results of this research can help decide if Thiol-SAMMS is a possible choice for remediation of the Berkeley Pit.

The Berkeley Pit was an open pit mine operated from 1955 to 1982. Groundwater and surface water runoff into the pit had to be continually pumped out while the mine was in operation. After the mine closed down in 1982, the pumps were shut down. Water began filling the pit and mixing with the metal contaminants in the mine. Today, the pit holds over 40 billion gallons of contaminated water, and the water level is currently at approximately 5,280 feet above sea level (PitWatch 2009). The U.S. Environmental Protection Agency (EPA) and the Montana Department of Health and Environmental Sciences set a critical water level (CWL) of 5,410 feet above sea level. If no remedial action is done, the CWL is estimated to be reached in 2015 (EPA 1994).

Thiol-SAMMS, developed at Pacific Northwest National Laboratory (PNNL), is the adsorbent tested in this research to remove dissolved metals from the Berkeley Pit water. Two types of tests, loading and kinetics, were performed. Loading tests were run to verify how many dissolved metals were adsorbed by Thiol-SAMMS after mixing with Berkeley Pit water for at least 24 hours. Kinetics tests were run to determine how fast Thiol-SAMMS adsorbed dissolved metals from Berkeley Pit water during a sampling period of 8 hours. The concentrations of four dissolved metals (aluminum, beryllium, copper, and zinc) were analyzed.

For the loading tests, five different ratios of Berkeley Pit water to Thiol-SAMMS (solution to solid) were tested. The ratios, in milliliters of Berkeley Pit water to grams of Thiol-SAMMS, were 5000:1, 1000:1, 500:1, 100:1, and 50:1. Berkeley Pit water was tested from both the surface and from a depth of 750 feet. In addition, because Berkeley Pit water is very acidic ($\text{pH} \approx 2.5$), samples were neutralized to $\text{pH} \approx 7$ either before addition of Thiol-SAMMS or after.

The results of the loading tests were analyzed by measuring and calculating the metal loading onto Thiol-SAMMS, which is a measure of how much metal is adsorbed per mass of Thiol-SAMMS. The results show that metal loading onto Thiol-SAMMS decreased proportionally with decreasing solution to solid ratio in post-neutralized Berkeley Pit water. However, for solutions neutralized before addition of Thiol-SAMMS, the neutralization step resulted in the majority of the metals forming solids and settling to the bottom of the solution before addition of Thiol-SAMMS.

For the kinetics tests, two solutions of Berkeley Pit water were tested. One was not neutralized, and the other was neutralized before the addition of Thiol-SAMMS. Only Berkeley Pit water from a depth of 750 feet was tested. In addition, the solution to solid ratio for each solution was 2000:1.

The results of the kinetics test in which the solution was not neutralized showed that no changes in the concentrations of the four metals were observed. This is likely due to the high acidity (low pH) of the solution and thus the high concentration of hydrogen ions in the solution. The hydrogen ions compete with dissolved metal ions for binding sites onto Thiol-SAMMS. Therefore, loadings observed in the post-neutralized loading tests were likely due to neutralization and not metal loading on Thiol-SAMMS. For the solution neutralized before the addition of Thiol-SAMMS, adsorption was confounded by the neutralization step, which resulted in the majority of the metals forming solids and settling to the bottom of the solution before Thiol-SAMMS was added.

This research shows that neutralization of the Berkeley Pit water removes a significant amount of dissolved metals, causing them to form solids and settle. Thiol-SAMMS is not effective in adsorbing contaminants at the low pH of the Berkeley Pit. However, neutralization followed by treatment with Thiol-SAMMS can bring down contaminant concentrations in Berkeley Pit water to below drinking water standards. Further research will help determine how well this combination of remedial techniques will work.

3. RESEARCH DESCRIPTIONS

Loading and kinetics tests were performed to determine the efficiency of adsorption of dissolved metals onto Thiol-SAMMS. The experimental procedure for each type of test is described in the following sections.

3.1 Loading Experiments

The loading experiments were run to determine how well Thiol-SAMMS adsorbed dissolved metals over a mixing period of at least 24 hours. Berkeley Pit water was tested both from the surface and from a depth of 750 feet. Different ratios of Berkeley Pit water (in milliliters) to Thiol-SAMMS (in grams) were run. For water from 750 feet deep, the ratios tested were 1000:1, 500:1, 100:1, and 50:1. For water from the surface, the same four ratios plus an additional ratio of 5000:1 were tested. In addition, because Berkeley Pit water is acidic ($\text{pH} \approx 2.5$), some solutions were neutralized before the addition of Thiol-SAMMS and some after. For each sample, a duplicate, and sometimes a triplicate, was run.

Table 1 shows the ratios of Berkeley Pit surface water to Thiol-SAMMS and the corresponding Berkeley Pit water volume and Thiol-SAMMS mass for each ratio.

Table 1. Ratios of Berkeley Pit surface water to Thiol-SAMMS

Ratio (mL:g)	Volume of surface Berkeley Pit water (mL)	Thiol-SAMMS (g)
5000:1	500	0.100
1000:1	125	0.125
500:1	62.5	0.125
100:1	25	0.250
50:1	12.5	0.250

Table 2 shows the ratios of Berkeley Pit water from a depth of 750 feet to Thiol-SAMMS and the corresponding Berkeley Pit water volume and Thiol-SAMMS mass for each ratio.

Table 2. Ratios of Berkeley Pit water from a depth of 750 feet to Thiol-SAMMS

Ratio (mL:g)	Volume of Berkeley Pit Water from 750 feet deep (mL)	Thiol-SAMMS (g)
1000:1	125	0.125
500:1	62.5	0.125
100:1	12.5	0.125
50:1	12.5	0.250

For each ratio of Berkeley Pit surface water to Thiol-SAMMS, two solutions were neutralized before addition of Thiol-SAMMS and two were neutralized after. Three samples of Berkeley Pit surface water were also taken: one without adding anything, one neutralized to a $\text{pH} \approx 7$, and one neutralized to a $\text{pH} \approx 8$. A total of twenty-three solutions were prepared for Berkeley Pit surface water.

For Berkeley Pit water from a depth of 750 feet, several solutions were run in triplicates because of potential uncertainty in volumetric measurements. Nonetheless, most of the solutions were run as duplicates. Six samples of Berkeley Pit water from a depth of 750 feet were also taken: two without adding anything, three neutralized to a $\text{pH} \approx 7$, and one neutralized to a $\text{pH} \approx 8$. A total of twenty-five solutions were prepared for Berkeley Pit water from 750 feet deep.

Each solution that was neutralized before addition of Thiol-SAMMS was prepared in the following way:

1. One or more volumetric flasks and a digital or manual pipette were used to obtain the required volume of Berkeley Pit (BP) water. For example, if the required amount was 500mL (as in the 5000:1 ratio), a volumetric flask of 500mL was used to measure the required volume. If the required amount was 62.5mL (as in the 500:1 ratio), one 50mL volumetric flask and one 10mL volumetric flask were used to measure out 60mL of BP water, and then either a digital or manual pipette was used to measure out the final 2.5mL for a total of 62.5mL. The entire measured quantity was then poured into a sample bottle.
2. Once the correct amount of BP water was in a sample bottle, the solution was neutralized with a 5M LiOH solution prepared using LiOH (Alfa Aesar). The 5M LiOH was added with a transfer pipette, and the pH was checked using pH strips (EMD colorpHast) until approximately a neutral pH was achieved.
3. A second sample bottle was prepared to hold the required amount of Thiol-SAMMS. The Thiol-SAMMS was weighed using a plastic weigh boat and an analytical balance (Mettler Toledo PR5003 DualRange). The Thiol-SAMMS was then transferred from the weigh boat to the second bottle.
4. Larger particles of Thiol-SAMMS in the second sample bottle were broken into smaller pieces by crushing with a metal spatula. This resulted in the particles of Thiol-SAMMS being all similar in size and allowing more particle surface area to react in solution. This was done for most of the tests on BP water from 750 feet deep and some of the tests for BP surface water.
5. Because Thiol-SAMMS is hydrophobic, it was preconditioned with ethanol (Sigma Aldrich) in order to allow it to function in BP water.
6. Once the Thiol-SAMMS was preconditioned in the second sample bottle, the solution in the first sample bottle was poured into the second sample bottle.
7. The bottle top threads were wrapped tight with Teflon tape and sealed with a bottle cap.

8. The solution was shaken with a mechanical shaker for 24 hours or more.
9. The mass of the solution and bottle was weighed using the analytical balance.
10. A 10mL volume of the solution was then taken up with a 10mL syringe. A syringe tip filter of 45 μ m was then added to the syringe. The first 5mL were returned to the sample bottle in order to prime the filter. The remaining 5mL were added to a scintillation vial. This was repeated to obtain 10 mL in total in the scintillation vial to be analyzed using ICP-MS for mercury and ICP-OES for more dissolved metals.
11. After the results from the lab for ICP-MS and ICP-OES came back, the solution was emptied and the bottle was cleaned.
12. The empty bottle, cap, and Teflon tape was then weighed using the analytical balance. This weight, along with the weight of Thiol-SAMMS in the solution, was subtracted from the weight of the solution with bottle and cap in order to obtain the Berkeley Pit water mass in each solution.
13. Using the density of Berkeley Pit water, the actual volume of Berkeley Pit water for each solution was calculated.
14. The results from the lab and the mass of Berkeley Pit water in each solution were used to calculate the loading for each solution.

For a solution neutralized after addition of Thiol-SAMMS, the preparation was similar. The difference was that the solution was neutralized after shaking for 24 hours, followed by taking a sample for analysis by ICP-MS and ICP-OES.

3.2 Kinetics Experiments

The kinetics experiments tested the speed at which Thiol-SAMMS adsorbed dissolved metals from Berkeley Pit water. Berkeley Pit water from a depth of 750 feet was used in the kinetics experiments. For each of the two solutions in the kinetics experiments, the ratio tested was 2000:1 (milliliters of Berkeley Pit water to grams of Thiol-SAMMS). One solution was neutralized before the addition of Thiol-SAMMS; the other was not neutralized. An initial sample was taken for each experiment. Once each experiment began, samples were collected at 2, 5, 10, 15, 30, 60, 120, 240, and 480 minutes after the beginning of the experiment.

The experimental procedure for the solution neutralized before adding Thiol-SAMMS is as follows:

1. One empty 2000mL bottle and cap were weighed with an analytical balance (Mettler Toledo PR5003 DualRange).
2. The volume of Berkeley Pit water required for each experiment was 1000mL. This volume was measured using a 1000mL volumetric flask.
3. The volume of Berkeley Pit water was then added to the bottle and weighed.

4. A solution of 5M LiOH, prepared from a solution of LiOH (Alfa Aesar), was added slowly to the Berkeley Pit water using a transfer pipette, and the pH was checked using pH strips (EMD colorpHast) until an approximately neutral pH was achieved.
5. A mass of 0.5g of Thiol-SAMMS was weighed using a weigh boat and the analytical balance.
6. A second 2000mL bottle and cap were weighed using the analytical balance.
7. The measured mass of Thiol-SAMMS was added to the second bottle, and the larger particles of Thiol-SAMMS were crushed with a metal spatula to allow more particle surface area to be exposed to the solution.
8. The bottle with the Thiol-SAMMS was weighed with the analytical balance. Teflon tape was added to the threads on the bottle top.
9. Using a transfer pipette, ethanol was added to the Thiol-SAMMS in order to precondition it to allow it to function in Berkeley Pit water.
10. A stopwatch was readied.
11. An initial sample of the solution was taken using a 10mL syringe. The syringe was used to collect 10mL of solution. Then, a 0.45 μ m syringe tip filter was placed on the syringe. The first 5mL were returned back to the solution in order to prime the filter. The remaining 5mL were added to a scintillation vial. This was repeated with a new filter to obtain a total of 10mL in the scintillation vial for a sample.
12. Once the experiment was ready to begin, the entire contents of the first bottle, which contained the neutralized Berkeley Pit water, were added to the second bottle, which contained the preconditioned Thiol-SAMMS. The stopwatch began.
13. The bottle was put in a mechanical shaker and shaken throughout the entire experiment, except when samples were being taken.
14. Samples were taken at 2, 5, 10, 15, 30, 60, 120, 240, and 480 minutes. For each time, a 10mL syringe was used to take 10mL of solution. A 0.45 μ m syringe tip filter was then added to the syringe and the first 5mL were returned to the solution in order to prime the filter. The remaining 5mL were added to a scintillation vial. This was repeated with a new filter to obtain a total of 10mL in the scintillation vial for each sample. For each time sampled, a new syringe was used.

The procedure for the unneutralized kinetics test was very similar except that it lacked the neutralization step.

In addition to the loading experiment and the kinetics experiment, a literature review on the Berkeley Pit and Thiol-SAMMS was completed to achieve a better understanding of the problem and the proposed method for remediation. The literature review on the design of Thiol-SAMMS helped in understanding the results.

4. RESULTS AND ANALYSIS

The results of the loading tests for Berkeley Pit water were analyzed by first calculating the loading for each solution. The loading is a measure of how much of a metal (in milligrams) is adsorbed onto each gram of Thiol-SAMMS. The equation for loading is as follows:

$$\text{Loading (mg Metal / g Thiol-SAMMS)} = (c_i - c_f)V_{\text{solution}} / m_{\text{Thiol-SAMMS}}$$

where c_i and c_f are the initial and final concentrations of the metal in solution in milligrams per liter, respectively, V_{solution} is the volume of the solution in liters, and $m_{\text{Thiol-SAMMS}}$ is the mass of Thiol-SAMMS added to the solution in grams. For solutions neutralized after addition of Thiol-SAMMS, the initial concentration is that of regular Berkeley Pit water. For solutions neutralized before addition of Thiol-SAMMS, the initial concentration is that of neutralized Berkeley Pit water.

The graph in Figure 2 displays the data for the loading experiment for Berkeley Pit surface water neutralized after addition of Thiol-SAMMS.

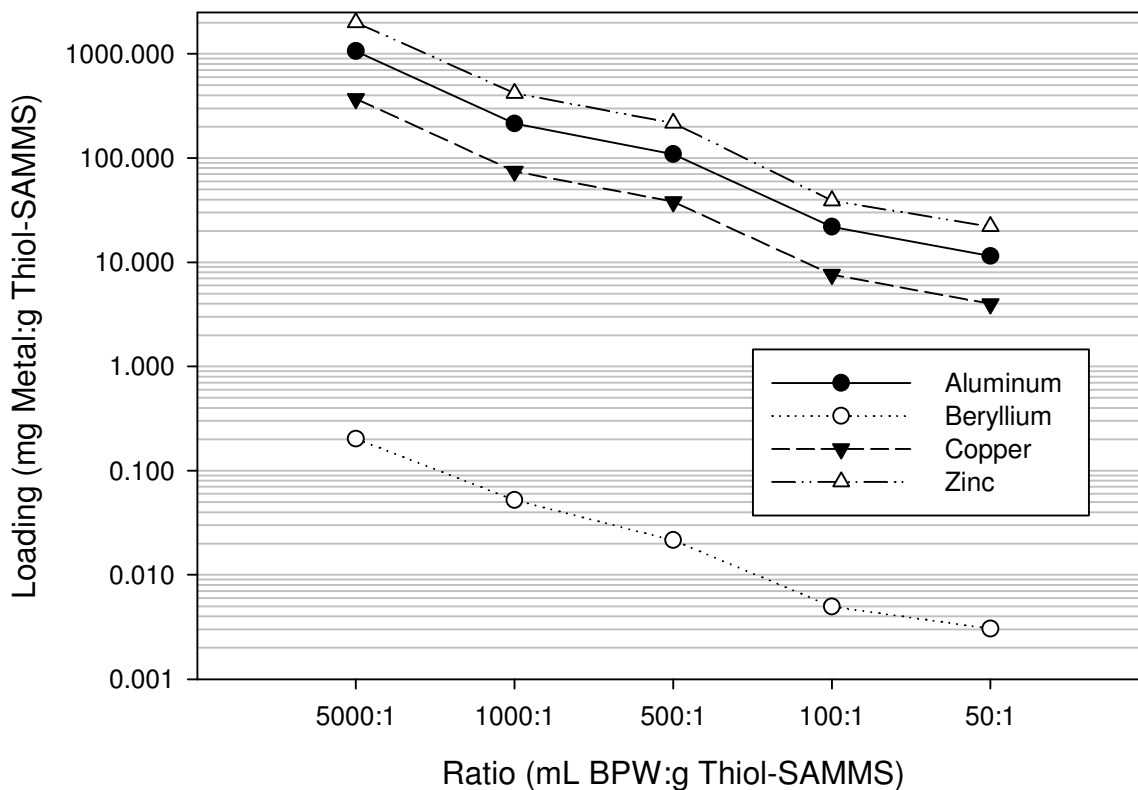


Figure 2. Loading experiment for Berkeley Pit surface water neutralized after addition of Thiol-SAMMS.

In Figure 2, BPW stands for Berkeley Pit water. From the data, it can be seen that for all four metals, the loading decreases proportionally with the decreasing Berkeley Pit water to Thiol-SAMMS (solution to solid) ratio. The graph shows that zinc is adsorbed the most, followed by aluminum and copper. Beryllium is adsorbed in a very small amount; this is due most likely to the small initial concentration of beryllium in Berkeley Pit water.

Figure 3 shows results of the loading experiment for Berkeley Pit surface water neutralized before addition of Thiol-SAMMS.

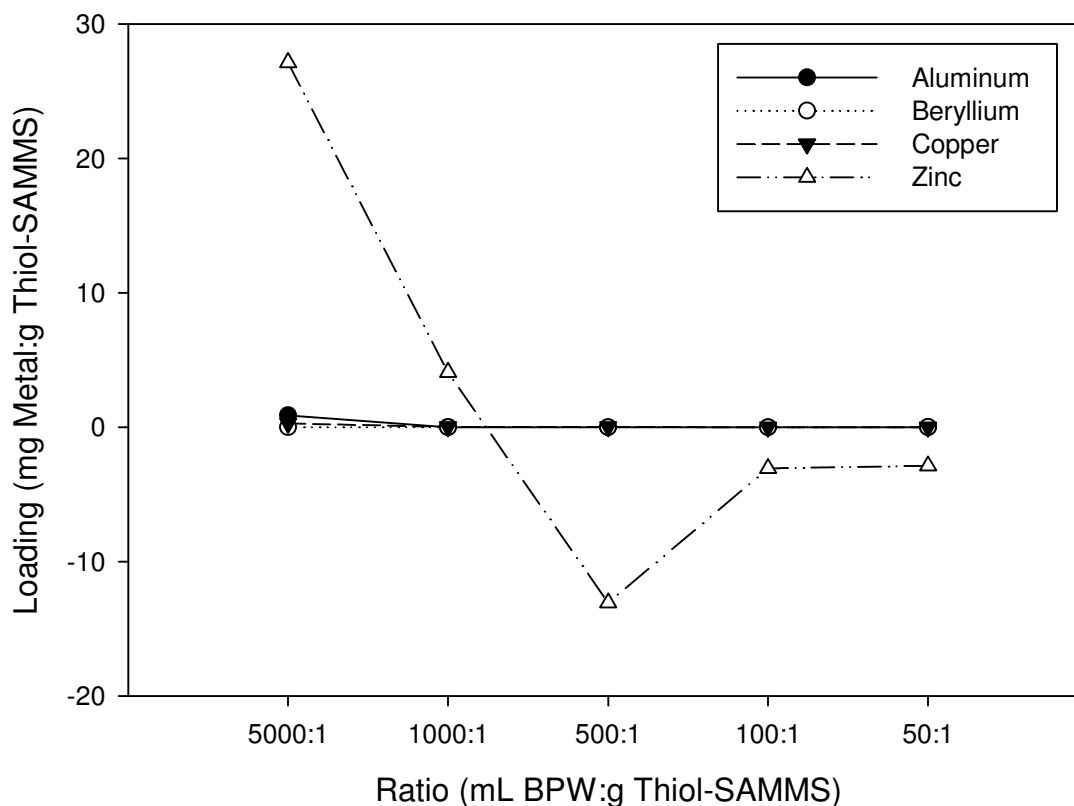


Figure 3. Loading experiment for Berkeley Pit surface water neutralized before addition of Thiol-SAMMS.

From Figure 3, it can be seen that the loadings for aluminum, beryllium, and copper are close to zero. This shows that the neutralization step removed the majority of these metal ions, leaving a very small amount for Thiol-SAMMS to adsorb. For zinc, the loading is above zero for the first two Berkeley Pit water to Thiol-SAMMS ratios, but then drops to negative values for the rest of the ratios. Loading cannot be negative. It is possible that the loading values for zinc fell below the detection limit of the ICP-OES instrument. However, a more likely explanation can be made after observing the data for the kinetics experiments.

Figure 4 shows the loading experiment for Berkeley Pit water from a depth of 750 feet neutralized after addition of Thiol-SAMMS.

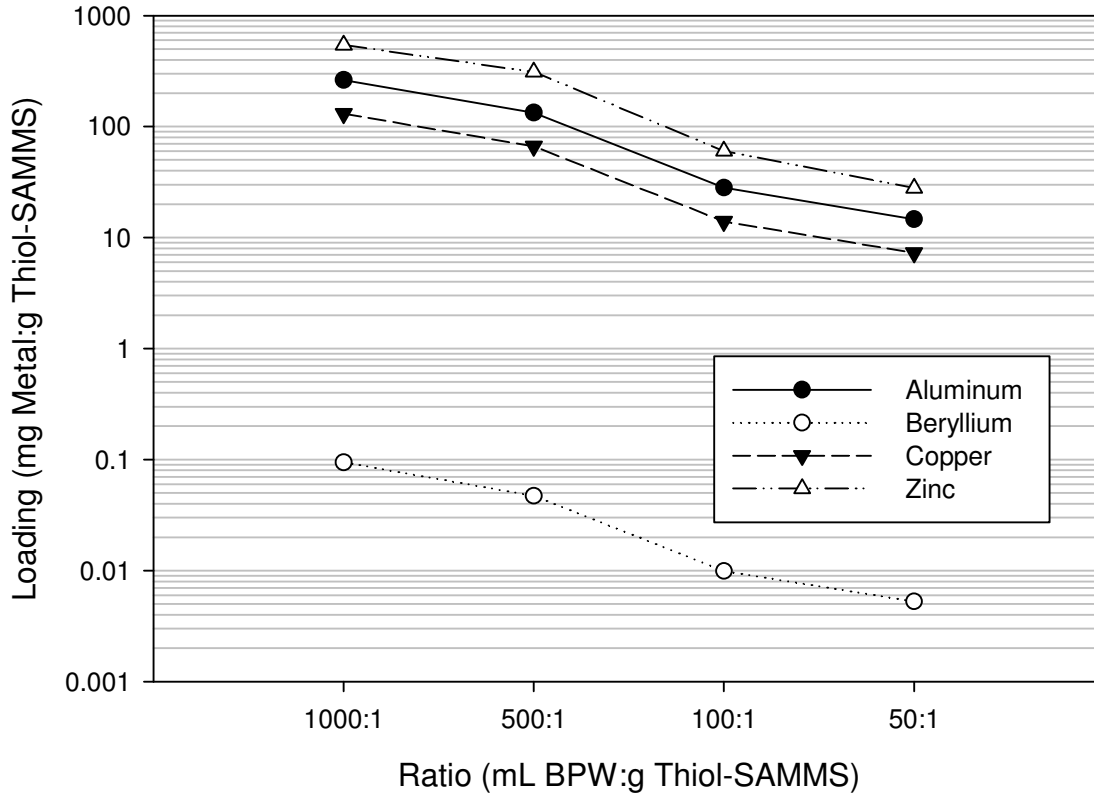


Figure 4. Loading experiment for Berkeley Pit water from 750 feet deep neutralized after addition of Thiol-SAMMS.

Berkeley Pit water from a depth of 750 feet, Figure 4, is very similar to Berkeley Pit surface water, Figure 2.

Figure 5 shows the loading experiment for Berkeley Pit water from a depth of 750 feet neutralized before addition of Thiol-SAMMS.

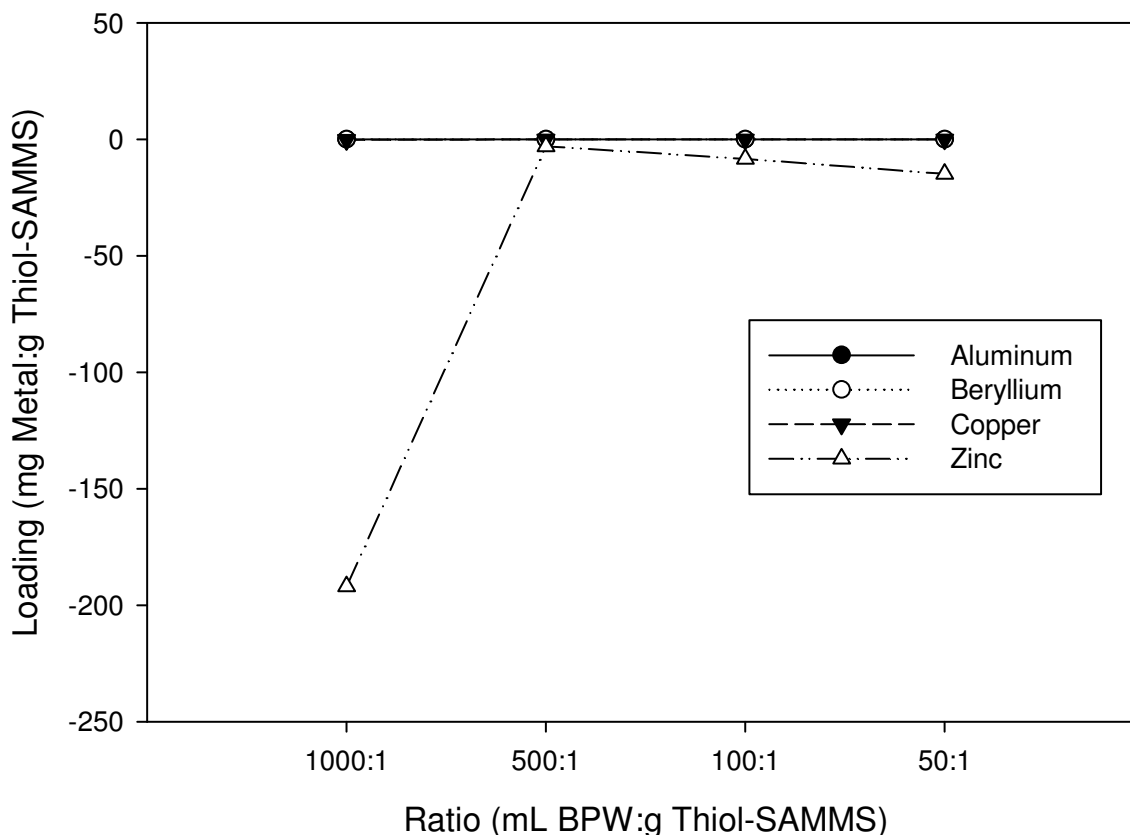


Figure 5. Loading experiment for Berkeley Pit water from 750 feet deep neutralized before addition of Thiol-SAMMS.

The loading experiment for Berkeley Pit water from a depth of 750 feet, neutralized before addition of Thiol-SAMMS, is similar to that of Berkeley Pit surface water. However, in the case of Berkeley Pit water from a depth of 750 feet, zinc concentration starts out at a negative number and approaches zero but remains negative for all four ratios. The zinc concentration may have been below the detection limit of the ICP-OES instrument. To have a better idea of what processes are occurring in the loading experiments, the kinetics experiments need to be analyzed too.

From the four graphs above, it is uncertain if the loadings observed in the two loading experiments for Berkeley Pit water neutralized after addition of Thiol SAMMS (Figure 2 and Figure 4) were due to the adsorbent or to neutralization. The kinetics experiments need to be analyzed as well

The graph in Figure 6 is for the kinetics experiment of Berkeley Pit water from a depth of 750 feet, neutralized before addition of Thiol-SAMMS.

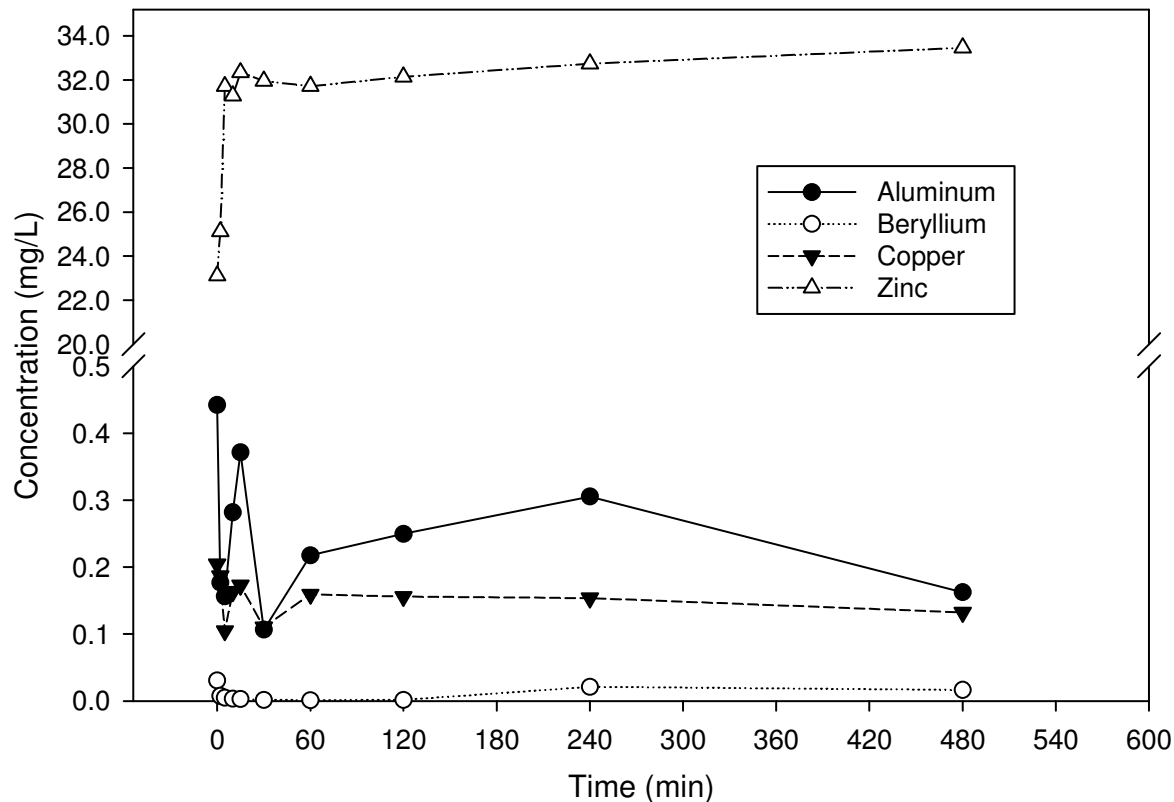


Figure 6. Kinetics experiment for Berkeley Pit water from 750 feet deep neutralized before addition of Thiol-SAMMS.

The kinetics graph for Berkeley Pit water neutralized before addition of Thiol-SAMMS (Figure 6) shows that the concentrations of aluminum, beryllium, and copper were very close to zero. The concentrations of these three metals fluctuated throughout the experiment. The fluctuations observed were all at concentrations below the detection limits of the ICP-OES instrument. The fluctuations may still have been present, however. If they were present, the fluctuations may have been caused by competition between the metal ions for adsorption onto Thiol-SAMMS. The initial concentration of each of these three metals was higher than the final concentrations. For zinc, however, the initial concentration was lower than the final concentration. Zinc concentration increased over time. Because Thiol-SAMMS releases hydrogen ions when metals bind to its surface (Feng et al. 1997), the hydrogen ion concentration in the solution may increase as more metals bind to Thiol-SAMMS. This will cause the pH to decrease. As the pH decreases, zinc that had solidified may dissolve back into solution. Figure 3 and Figure 5 showed negative loadings for zinc. This may have been caused by zinc dissolving back into solution.

Figure 7 shows the kinetics experiment for Berkeley Pit water from a depth of 750 feet, not neutralized.

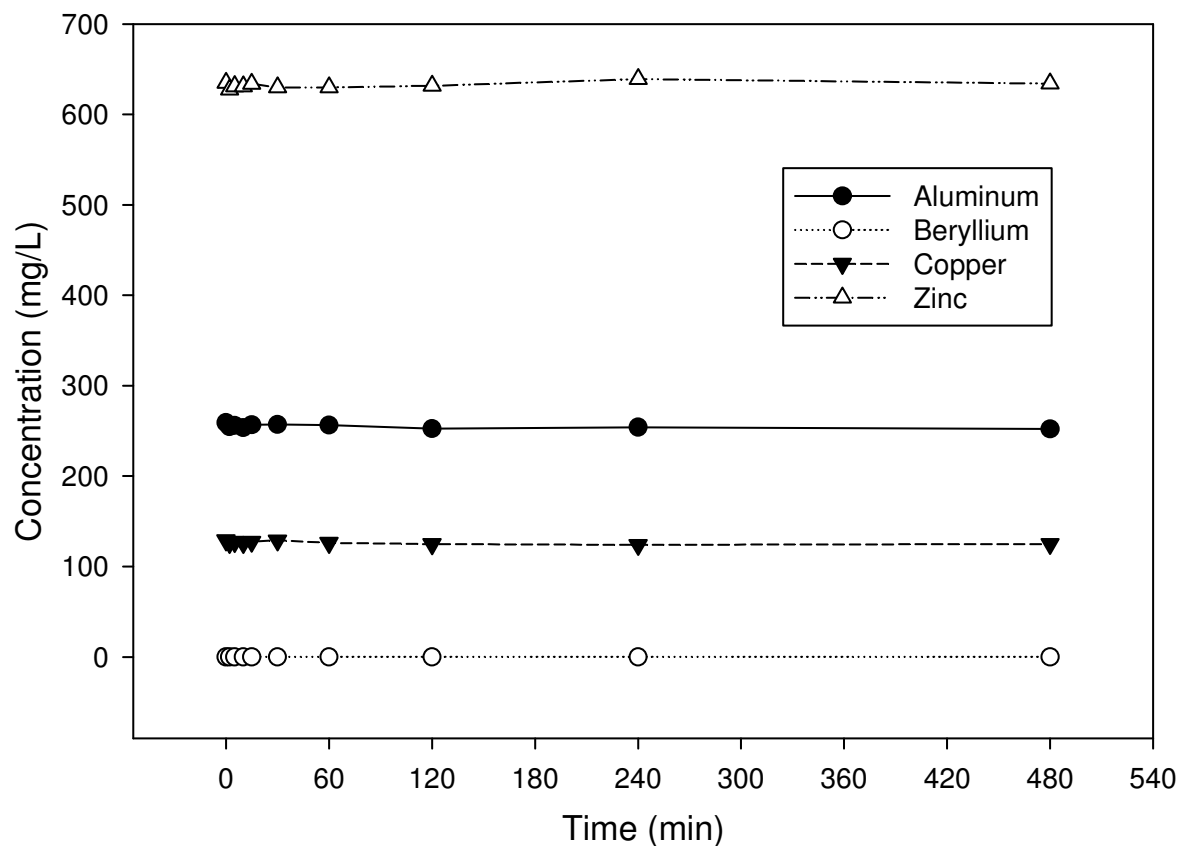


Figure 7. Kinetics experiment for unneutralized Berkeley Pit water from 750 feet deep

The kinetics graph for unneutralized Berkeley Pit water shows that no changes in concentration for any of the metals were observed. Because the Berkeley Pit water is very acidic, there is a high concentration of hydrogen ions in solution. These hydrogen ions compete with metal ions in solution to adsorb onto Thiol-SAMMS. In addition, because no changes in concentrations were observed in the kinetics experiment for unneutralized Berkeley Pit water, the loadings observed in the loading experiments for Berkeley Pit water neutralized after the addition of Thiol-SAMMS were likely due to neutralization and not metal loading onto Thiol-SAMMS.

5. CONCLUSION AND FUTURE WORK

A large amount of the dissolved metals in Berkeley Pit water can be removed by neutralization. Thiol-SAMMS cannot function in the highly acidic Berkeley Pit water. Nevertheless, if neutralization is followed by Thiol-SAMMS, this combination of techniques can bring down contaminant levels to below drinking water standards. Future research is necessary to verify this. In the kinetics experiment for Berkeley Pit water neutralized before addition of Thiol-SAMMS, the majority of dissolved metals solidified and settled to the bottom of the bottle. These solids were not removed from the bottle. This may have caused zinc, and possibly other metals, to dissolve back into solution upon addition of Thiol-SAMMS. When Thiol-SAMMS bonds to metal ions, it releases hydrogen ions, which may decrease pH of the solution. It is this drop in pH which may have been the reason that zinc dissolved back into solution. Future work can include a set of loading and kinetics experiments where the solids layer is removed. This would simplify the processes inside the solution by removing sediment feedback. This would also allow for an understanding of whether or not increased dissolved metal concentration (as in the case of zinc in this research) was caused by sediment feedback or competition between metal ions for binding sites on Thiol-SAMMS.

Figure 8 shows the three types of solutions possible in the kinetics and loading experiments. Future research will include a solution run with the solids layer removed before adding Thiol-SAMMS.

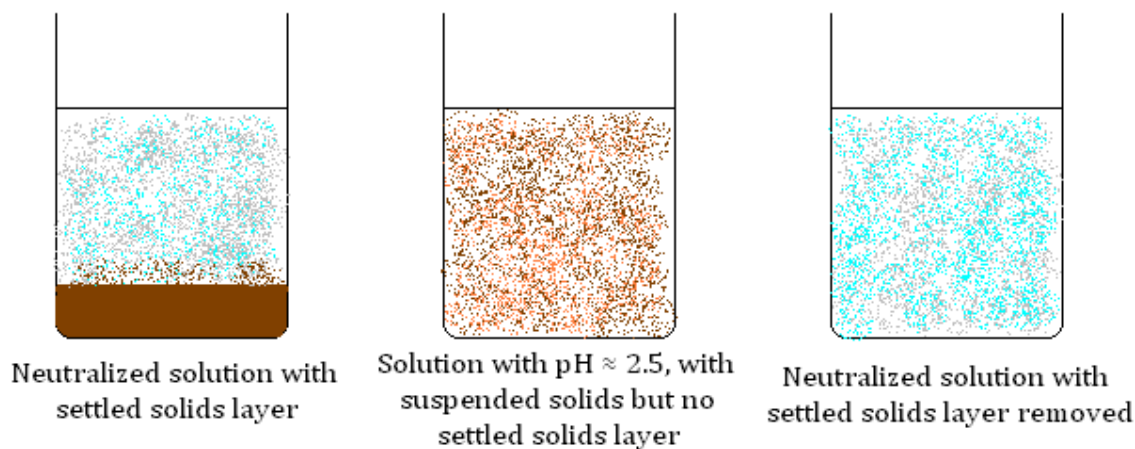


Figure 8. Three types of kinetics and loading experiments; for this research, the neutralized scenario with the solids layer and the non-neutralized scenario were both run. Future research should include the scenario on the right with the solids layer removed before adding Thiol-SAMMS.

The results of the experiments show that there may be competition between metal ions for binding sites on Thiol-SAMMS. Future research can include experiments designed to show competition between different metal species. Solutions can be created with only

two species present at first in order to determine the competition between both species. Then, more types of metal ions may be added one at a time to show the competition between three or more metal ions for binding sites on Thiol-SAMMS.

The results also show that zinc concentration increased over time in the kinetics experiment of Berkeley Pit water neutralized before addition of Thiol-SAMMS. This increase in concentration may have been caused by a decrease in the pH of solution. This decrease in pH was probably caused by metal loading onto Thiol-SAMMS. Future experiments can be designed to improve measuring the pH of solution. This will allow the researcher to verify the pH change of solution upon adding Thiol-SAMMS.

In addition, Thiol-SAMMS may be added to a computer model to help in understanding metal loading onto Thiol-SAMMS at different conditions. If the computer model is reliable and has been tested and verified for numerous conditions with known concentrations, a better understanding of metal loading onto Thiol-SAMMS can be achieved.

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APPENDIX A: Loading Data

Table 3 shows the loadings from the loading experiment for Berkeley Pit surface water. The loadings are calculated for aluminum, beryllium, copper, and zinc. The first number in the bottle ID represents the Berkeley Pit water to Thiol-SAMMS (solution to solid) ratio, where 0 is the first ratio, 5000:1, and 4 is the last ratio, 50:1. A bottle ID with “NB” means that solution was neutralized before addition of Thiol-SAMMS, and “NA” means neutralized after. For each solution, a duplicate was run.

Table 3. Loadings for Berkeley Pit surface water

	Loading Aluminum	Loading Beryllium	Loading Copper	Loading Zinc
Bottle ID	mg Al / g adsorbent	mg Be / g adsorbent	mg Cu / g adsorbent	mg Zn / g adsorbent
0NB1	0.68763735	3.5914E-05	0.365080291	28.3548603
0NB2	1.10513681	0.00152374	0.183384552	25.9208298
0NA1	1058.14323	0.27123368	368.7036353	2082.94978
0NA2	1068.03307	0.13362491	371.3043428	1906.08941
1NB1	-0.0012069	-0.017514	0.019802798	5.15386705
1NB2	0.01750779	-0.0064075	0.016124019	3.03838026
1NA1	214.001069	0.05251848	74.56298241	414.8495
1NA2	214.208273	0.05164278	74.53376501	423.484507
2NB1	0.08039705	-0.0014803	0.018084705	-15.7203125
2NB2	-0.0931227	-0.0005299	0.015049502	-10.4121102
2NA1	108.822556	0.02803703	37.90601524	215.944297
2NA2	109.289966	0.01480305	38.03990502	216.989133
3NB1	-0.0085435	-0.0014838	-0.002827228	0.5374433
3NB2	0.00789136	-0.001105	-0.000100601	-6.65240693
3NA1	21.7148811	0.00461704	7.548372493	34.8562994
3NA2	22.0740625	0.00531075	7.684278331	43.0720471
4NB1	0.0016446	2.6518E-05	0.00207152	-0.21582085
4NB2	-0.0010239	7.3101E-05	0.003663042	-5.54639185
4NA1	11.6575047	0.00309804	4.060044149	21.8091666
4NA2	11.2262204	0.00297831	3.914467716	22.1644608
Berk Pit Surface H2O	N/A	N/A	N/A	N/A
Berk Pit Surface H2O, pH~7	N/A	N/A	N/A	N/A
Berk Pit Surface H2O, pH~8	N/A	N/A	N/A	N/A

Table 4 shows the loadings from the loading experiment for Berkeley Pit water from a depth of 750 feet. The “BPW 750” in the bottle ID means that the Berkeley Pit water comes from a depth of 750 feet. The ratio follows the “BPW 750”. In the Bottle ID, “NA” stands for neutralized after addition of Thiol-SAMMS, and “NB” stands for neutralized before. For each solution, a duplicate was also run.

Table 4. Loadings for Berkeley Pit water from 750 feet deep

	Loading Aluminum	Loading Beryllium	Loading Copper	Loading Zinc
Bottle ID	mg Al / g adsorbent	mg Be / g adsorbent	mg Cu / g adsorbent	mg Zn / g adsorbent
BPW 750 1000:1/NA1	264.864	0.096	131.820	658.267
BPW 750 1000:1/NA2	261.273	0.092	129.522	429.866
BPW 750 1000:1/NB1	-0.017	0.009	-0.364	-207.376
BPW 750 1000:1/NB2	-0.051	-0.017	-0.240	-176.737
BPW 750 500:1/NA1	133.245	0.047	66.302	293.978
BPW 750 500:1/NA2	133.082	0.047	66.182	326.950
BPW 750 500:1/NB1	-0.015	-0.001	0.034	-5.187
BPW 750 500:1/NB2	-0.010	0.001	-0.022	-0.861
BPW 750 100:1/NA1	28.379	0.011	14.128	70.286
BPW 750 100:1/NA2	28.227	0.011	14.004	52.532
BPW 750 100:1/NA3	27.695	0.008	13.758	57.488
BPW 750 100:1/NB1	-0.006	0.001	0.002	-0.861
BPW 750 100:1/NB2	-0.013	0.001	0.000	-5.933
BPW 750 100:1/NB3	-0.013	0.001	-0.031	-18.471
BPW 750 50:1/NA1	14.626	0.005	7.270	27.139
BPW 750 50:1/NA2	14.635	0.005	7.279	22.988
BPW 750 50:1/NA3	14.593	0.005	7.263	33.622
BPW 750 50:1/NB1	-0.014	0.000	-0.002	-5.900
BPW 750 50:1/NB2	-0.095	0.000	-0.016	-23.715
BPW 750 - 1	N/A	N/A	N/A	N/A
BPW 750 - 2	N/A	N/A	N/A	N/A
BPW 750 - 1pH7	N/A	N/A	N/A	N/A
BPW 750 - 2pH7	N/A	N/A	N/A	N/A
BPW 750 - 2pH8	N/A	N/A	N/A	N/A
BPW 750 - 3pH7	N/A	N/A	N/A	N/A

APPENDIX B: Experiment Data

Table 5 shows the density testing for deionized water, Berkeley Pit surface water, and Berkeley Pit water from a depth of 750 feet.

Table 5. Density calculations of deionized water, Berkeley Pit surface water, and Berkeley Pit water from a depth of 750 feet.

Volumetric Flask with cap Tare Weight	Volumetric Flask with cap Tare Weight plus 10 mL Deionized (DI) water	Mass of DI Water (Room Temperature)
g	g	g
11.830	21.736	9.906
11.830	21.737	9.907
11.830	21.749	9.919
Volumetric Flask with cap Tare Weight	Volumetric Flask with cap Tare Weight plus 10 mL Berkeley Pit Water (BPW) from the Surface	Mass of Berkeley Pit Water (Relatively cold ~ 50°F)
g	g	g
11.849	21.856	10.007
11.833	21.854	10.021
11.829	21.862	10.033
11.829	21.842	10.013
Volumetric Flask with cap Tare Weight	Volumetric Flask with cap Tare Weight plus 10 mL Berkeley Pit Water (BPW) from 750 feet	Mass of Berkeley Pit Water
g	g	g
11.812	21.856	10.044
11.811	21.885	10.074
11.809	21.872	10.063
Average Density of DI Water	0.991	g/mL
Average Density of Berkeley Pit Water from the Surface	1.002	g/mL
Average Density of Berkeley Pit Water from 750 feet	1.006	g/mL

Table 6 shows the results of the kinetics experiment for Berkeley Pit water neutralized before addition of Thiol-SAMMS. The number in between “BPW” and “NB” is the sample time in minutes after the beginning of the experiment. The number after “NB” means that a single sample was taken and no duplicate was run.

On June 30, 2009, an initial sample was taken before the experiment began, and then the solution of neutralized Berkeley Pit water was added to the Thiol-SAMMS; however, the Thiol-SAMMS was not preconditioned. The Thiol-SAMMS rose to the top of the solution and was removed with a spatula, a transfer pipette, and Kim wipes. On July 1, 2009, the kinetics experiment was restarted. Accidentally, an initial sample was not taken. Only a very small amount of the initial sample was left in its original bottle, possibly too little for the ICP-MS and ICP-OES instruments to use. The results of the initial sample from June 30 and the small amount of sample from July 1 were averaged to obtain the estimated initial concentration of the solution. The average initial concentration is on the line for June 30, 2009.

Table 6. Concentrations of aluminum, beryllium, copper, and zinc for the kinetics experiment for Berkeley Pit water neutralized before addition of Thiol-SAMMS

Sample Name	Time (min)	Aluminum Concentration (ppm)	Beryllium Concentration (ppm)	Copper Concentration (ppm)	Zinc Concentration (ppm)
BPW 0 NB(1) - 06/30	0	0.4421646	0.030668775	0.2046117	23.10556
BPW 0 NB(1) - 07/01					
BPW 2 NB(1)	2	0.1765924	0.007337692	0.1869016	25.11291
BPW 5 NB(1)	5	0.1564282	0.00490218	0.1046386	31.71235
BPW 10 NB(1)	10	0.2818052	0.003357555	0.1630868	31.28213
BPW 15 NB(1)	15	0.3713849	0.002726821	0.1726401	32.33618
BPW 30 NB(1)	30	0.106379	0.001595676	0.1102508	31.95165
BPW 60 NB(1)	60	0.2175206	0.001049263	0.1592367	31.71475
BPW 120 NB(1)	120	0.2496586	0.0015524	0.1559334	32.14023
BPW 240 NB(1)	240	0.305322	0.02108043	0.1535105	32.73715
BPW 480 NB(1)	480	0.1622285	0.01646579	0.1322466	33.4606

The results for the kinetics experiment for unneutralized Berkeley Pit water are provided in Table 7.

Table 7. Concentrations of aluminum, beryllium, copper, and zinc for the kinetics experiment for unneutralized Berkeley Pit Water

Sample Name	Time	Aluminum Concentration (ppm)	Beryllium Concentration (ppm)	Copper Concentration (ppm)	Zinc Concentration (ppm)
BPW 0 NN(1)	0	259.067	0.09489327	129.0551	634.9606
BPW 2 NN(1)	2	254.8589	0.09129032	126.2303	627.2307
BPW 5 NN(1)	5	256.0634	0.09028966	127.2933	631.1288
BPW 10 NN(1)	10	253.5512	0.09159052	126.0091	630.9998
BPW 15 NN(1)	15	256.7135	0.08829305	127.4844	633.9569
BPW 30 NN(1)	30	257.1584	0.08717663	128.8888	629.7477
BPW 60 NN(1)	60	256.3013	0.1164883	126.1333	629.8477
BPW 120 NN(1)	120	252.5142	0.1047443	124.7745	631.6557
BPW 240 NN(1)	240	254.113	0.1027221	123.9271	639.0899
BPW 480 NN(1)	480	252.0795	0.09923098	124.9866	633.9855

The following four tables (Tables 8 – 11) show data for the loading experiments for Berkeley Pit surface water and Berkeley Pit water from a depth of 750 feet. These data were used to calculate the loading of each metal onto Thiol-SAMMS.

Table 8. Masses used to calculate Berkeley Pit surface water mass

	Bottle and Cap Tare Weight	Ratio of volume of Berkeley Pit Water to mass of Thiol SAMMS	Bottle and Cap Tare Weight plus solution	Mass of Thiol SAMMS added	Mass of Berkeley Pit Water plus Thiol SAMMS	Mass of Berkeley Pit surface water only
Bottle ID	g	mL:g	g	g	g	g
0NB1	101.824	2000:1	607.358	0.101	505.534	505.433
0NB2	109.629	2000:1	616.654	0.100	507.025	506.925
0NA1	102.315	2000:1	603.951	0.101	501.636	501.535
0NA2	107.429	2000:1	608.428	0.100	500.999	500.899
1NB1	46.682	1000:1	173.755	0.125	127.073	126.948
1NB2	46.624	1000:1	172.372	0.128	125.748	125.620
1NA1	46.626	1000:1	172.210	0.125	125.584	125.459
1NA2	46.383	1000:1	172.061	0.125	125.678	125.553
2NB1	16.230	500:1	79.757	0.125	63.527	63.402
2NB2	15.718	500:1	79.066	0.126	63.348	63.222
2NA1	16.780	500:1	80.710	0.125	63.930	63.805
2NA2	16.299	500:1	79.973	0.124	63.674	63.550
3NB1	14.792	100:1	40.861	0.250	26.069	25.819
3NB2	14.769	100:1	40.345	0.250	25.576	25.326
3NA1	14.436	100:1	40.235	0.251	25.799	25.548
3NA2	14.916	100:1	41.052	0.250	26.136	25.886
4NB1	11.391	50:1	25.386	0.250	13.995	13.745
4NB2	11.297	50:1	25.833	0.250	14.536	14.286
4NA1	11.391	50:1	25.322	0.250	13.931	13.681
4NA2	11.154	50:1	24.579	0.250	13.425	13.175
Berk Pit Surface H2O	11.331	N/A	21.442	N/A	N/A	10.111
Berk Pit Surface H2O, pH~7	11.347	N/A	36.457	N/A	N/A	25.110
Berk Pit Surface H2O, pH~8	11.301	N/A	36.424	N/A	N/A	25.123

Table 9. Concentrations of aluminum, copper, beryllium, and zinc in parts per million for the loading experiment for Berkeley Pit surface water

	Aluminum Concentration (LAB)	Copper Concentration (LAB)	Beryllium Concentration (LAB)	Zinc Concentration (LAB)
Bottle ID	ppm (mg/L)	ppm (mg/L)	ppm (mg/L)	ppm (ug/L)
0NB1	0.08461594	0.07649303	0.01071047	0.2715269
0NB2	0.003868534	0.1133387	0.01041652	0.8253172
0NA1	0.2597392	0.1020709	0.009414234	4.631095
0NA2	0.1269989	0.2248968	0.03741043	43.63753
1NB1	0.2234704	0.1300465	0.02799478	0.863953
1NB2	0.2044073	0.1331216	0.01725859	2.84645
1NA1	0.1321149	0.06199431	0.01171366	10.77879
1NA2	0.0853704	0.1468599	0.01262636	2.475941
2NB1	0.06348002	0.1138607	0.01364154	36.99879
2NB2	0.4082145	0.1195327	0.01177567	26.73761
2NA1	0.1566627	0.09078494	0.009107998	1.037347
2NA2	0.1014748	0.1281003	0.03519936	0.6984912
3NB1	0.305158	0.1770076	0.02511161	0.7345441
3NB2	0.1442379	0.1505764	0.02164521	71.73737
3NA1	0.009046804	0.1923528	0.01869214	81.79094
3NA2	0.1649701	0.1396408	0.01275211	8.127437
4NB1	0.1923117	0.1118341	0.01023444	9.880828
4NB2	0.2402301	0.08536095	0.009436053	103.1876
4NA1	0.326985	0.1610762	0.007420013	25.60772
4NA2	0.3293507	0.07388031	0.007517797	3.519127
Berk Pit Surface H2O	213.7447	74.48962	0.0641368	424.8752
Berk Pit Surface H2O, pH~7	0.2222798	0.1495815	0.01071766	5.948123
Berk Pit Surface H2O, pH~8	0.217776	0.1672178	0.009930165	0.6761061

Table 10. Masses used to calculate mass of Berkeley Pit water from a depth of 750 Feet

	Bottle and Cap Tare Weight	Ratio of Berkeley Pit Water to Thiol SAMMS	Bottle and Cap Tare Weight plus solution	Mass of Thiol SAMMS added	Mass of Berkeley Pit Water plus Thiol SAMMS	Mass of Berkeley Pit Water (750') only
Bottle ID	g	(mL:g)	g	g	g	g
BPW 750 1000:1/NA1	46.803	1000:1	173.686	0.125	126.883	126.758
BPW 750 1000:1/NA2	44.327	1000:1	169.455	0.125	125.128	125.003
BPW 750 1000:1/NB1	46.956	1000:1	174.921	0.127	127.965	127.838
BPW 750 1000:1/NB2	46.669	1000:1	173.844	0.125	127.175	127.050
BPW 750 500:1/NA1	26.366	500:1	90.271	0.125	63.905	63.780
BPW 750 500:1/NA2	26.310	500:1	90.104	0.125	63.794	63.669
BPW 750 500:1/NB1	16.319	500:1	80.579	0.125	64.260	64.135
BPW 750 500:1/NB2	16.659	500:1	80.937	0.125	64.278	64.153
BPW 750 100:1/NA1	11.333	100:1	25.047	0.125	13.714	13.589
BPW 750 100:1/NA2	11.277	100:1	24.915	0.125	13.638	13.513
BPW 750 100:1/NA3	11.385	100:1	24.663	0.124	13.278	13.154
BPW 750 100:1/NB1	11.331	100:1	25.004	0.124	13.673	13.549
BPW 750 100:1/NB2	11.302	100:1	24.848	0.126	13.546	13.420
BPW 750 100:1/NB3	11.285	100:1	24.915	0.126	13.630	13.504
BPW 750 50:1/NA1	11.314	50:1	25.573	0.250	14.259	14.009
BPW 750 50:1/NA2	11.252	50:1	25.589	0.251	14.337	14.086
BPW 750 50:1/NA3	11.289	50:1	25.511	0.250	14.222	13.972
BPW 750 50:1/NB1	11.285	50:1	25.493	0.249	14.208	13.959
BPW 750 50:1/NB2	11.275	50:1	25.743	0.251	14.468	14.217
BPW 750 - 1	11.311	N/A	41.220	N/A	N/A	29.909

BPW 750 - 2	11.272	N/A	41.203	N/A	N/A	29.931
BPW 750 - 1pH7	11.276	N/A	41.948	N/A	N/A	30.672
BPW 750 - 2pH7	11.376	N/A	41.731	N/A	N/A	30.355
BPW 750 - 2pH8	11.296	N/A	41.728	N/A	N/A	30.432
BPW 750 - 3pH7	11.310	N/A	41.640	N/A	N/A	30.330

Table 11. Concentrations of aluminum, beryllium, copper, and zinc for the loading experiment for Berkeley Pit water from a depth of 750 feet

	Aluminum Concentration (LAB)	Beryllium Concentration (LAB)	Copper Concentration (LAB)	Zinc Concentration (LAB)
Bottle ID	ppm	ppm	ppm	ppm
BPW 750 1000:1/NA1	0.185	0.010	0.159	0.494
BPW 750 1000:1/NA2	0.109	0.012	0.635	221.100
BPW 750 1000:1/NB1	0.186	0.009	0.530	209.897
BPW 750 1000:1/NB2	0.220	0.034	0.404	177.572
BPW 750 500:1/NA1	0.235	0.013	0.208	73.917
BPW 750 500:1/NA2	0.098	0.012	0.217	7.782
BPW 750 500:1/NB1	0.199	0.020	0.101	12.808
BPW 750 500:1/NB2	0.189	0.016	0.209	4.326
BPW 750 100:1/NA1	0.329	0.005	0.190	3.113
BPW 750 100:1/NA2	0.269	0.004	0.607	164.679
BPW 750 100:1/NA3	0.304	0.029	0.463	108.354
BPW 750 100:1/NB1	0.220	0.008	0.146	10.566
BPW 750 100:1/NB2	0.288	0.007	0.166	58.674
BPW 750 100:1/NB3	0.292	0.006	0.453	176.026
BPW 750 50:1/NA1	0.360	0.013	0.411	166.314
BPW 750 50:1/NA2	0.590	0.010	0.447	241.447
BPW 750 50:1/NA3	0.263	0.009	0.189	48.318
BPW 750 50:1/NB1	0.419	0.018	0.197	108.515
BPW 750 50:1/NB2	1.861	0.015	0.459	423.849
BPW 750 - 1	262.713	0.092	131.332	652.748
BPW 750 - 2	263.190	0.118	130.537	654.349
BPW 750 - 1pH7	0.135	0.022	0.140	0.322
BPW 750 - 2pH7	0.266	0.017	0.181	0.936
BPW 750 - 2pH8	0.167	0.011	0.119	4.072
BPW 750 - 3pH7	0.107	0.013	0.179	6.655