The Effects of Restoring Tidal Circulation to Diked Salt Marshes on Alkalinity Generation and Sediment Profiles of Metals and Sulfur

Christine McCarthy  
Lafayette College  
730 High Street, Easton, PA 18042

Advisor: Dr. Anne Giblin  
Ecosystems Center  
Marine Biological Laboratory  
7 MBL Street, Woods Hole, MA 02543

Semester in Environmental Science  
Independent Project, 2014

Abstract

I explored the effects of diking and restoration of tidal circulation to salt marshes by analyzing depth profiles of carbon, sulfur, and iron in sediment cores, and pH and iron content in pore water from the Long Creek Salt Marsh in the East Sandwich Game Farm in East Sandwich, MA. I then conducted a water addition microcosm experiment to analyze the short term effects of the introduction of fresh and salt water to sediment cores from a site impounded and cut off from tidal circulation. Sediment chemistry characteristics of natural marsh and restored marsh cores indicated that restoration and the reintroduction of tidal circulation can indeed return a diked marsh to its original state. After adding fresh water and draining sediment cores from a marsh impacted by diking, pH of pore water decreases and iron leaches out of the core in the pore water in response to the oxidation of iron and sulfur in the sediment. The addition of seawater, however, generates alkalinity as it supplies a marsh with sulfur and other inorganic matter to neutralize acidity. Studying the response of diked salt marshes to restoration can give valuable information about resulting water quality and possible effects on the surrounding environment that are essential to management decisions.

Key Words

salt marsh restoration, Cape Cod, diking, restoration, salt marshes, sulfur cycling, alkalinity,  
_Spartina alterniflora, Phragmites australis_
Introduction

In many areas on Cape Cod, Massachusetts, the diking and drainage of coastal salt marshes have been practiced for hundreds of years. Man has empoldered these wetlands for the construction of roads and railways, for insect control, and for agricultural purposes, by restricting saltwater tidal flow into these areas. Recently, efforts have been made to restore diked salt marshes to their original state as negative effects of diking have become increasingly apparent. Such effects include vegetation change, water quality problems, pest insect outbreaks, and reduced fish and wildlife use (Biogeochemical 1997). Salt marshes in their original state also act as a spatial buffer between land and sea, a role that will become increasingly important with respect to sea level rise and that has further encouraged managers to pursue restoration.

We obtained and analyzed sediment cores from adjacent marshes of various degrees of impaction from diking to explore how diking affects salt marsh sediment characteristics. Specifically, I analyzed depth profiles of carbon, sulfur, and iron in the salt marsh sediments. These characteristics play an important role in the structure and function of salt marsh peat. The reduction of seawater flow to a salt marsh allows the surface water and pore water to freshen. Physical and chemical changes to salt marsh sediments are then dependent on whether they remain waterlogged or are drained (Biogeochemistry 1997). In drained marshes, specifically, the water table can drop to the groundwater level, which aerates the peat. This change in salinity and saturation affects the biogeochemistry of the marsh sediments. Oxidation of sulfur and iron in the sediment increases with aeration, which can result in salt marsh creeks becoming very acidic. This change in redox state and decreased pH can also alter the mobility of nutrients and metals within the sediment and pore water of the marsh, and can decrease oxygen concentrations in the water column, providing a positive feedback on the salt marsh ecosystem that can have negative impacts (Effects 1997). By comparing sediment cores from a natural marsh to those of a marsh that has been reintroduced to seawater circulation after a period of diking, I was able to make some judgments as to whether the reintroduction of tidal circulation can indeed return a diked marsh to its original condition.

We then conducted a microcosm experiment to mimic the short term effects of introducing fresh and salt water to salt marsh sediment. Specifically, I analyzed the response of pH, alkalinity, and iron concentration in pore water, and the change in sediment chemistry as a result of the experiment.
Study Site

All sediment cores and surface water samples were obtained from the Long Creek salt marsh in the East Sandwich Game Farm in East Sandwich, MA. The marsh is part of a 133 acre conservation area that once functioned as a ship yard, and then as a game farm for quails and pheasants for distribution throughout the state of Massachusetts. The farm ended its operation in 1987, and the land is now maintained by the Thornton W. Burgess Society (East Sandwich).

We identified three adjacent marsh sites along Long Creek to show characteristics of degrees of impaction by diking or restoration of seawater flow. Closest spatially to Cape Cod Bay is a natural, unaltered marsh site with a surface water salinity of 25 psu (unimpacted). This site was mainly inhabited by Spartina alterniflora with some Spartina patens, both of which are plants characteristic of salt water marshes. Moving away from Cape Cod Bay, a lightly traveled car bridge marks the separation of the unimpacted site from the restored site (Figure 1). Beneath the bridge, a large opening allows the channel to flow freely. This formerly diked marsh was restored to seawater circulation in 2006 (East Sandwich). With a surface water salinity of 13 psu, this site had some Phragmites australis, a plant characteristic to fresh water marshes, along the edges of the marsh with Spartina alterniflora closest to the main channel. Moving farther away from Cape Cod Bay, a railroad separates the restored site from the impacted site. Only a small culvert below the railroad allows some water flow between the impacted and restored marshes, so the impacted marsh showed characteristics of being almost completely cut off from tidal circulation. This site was inhabited mainly by Phragmites australis and had a surface water salinity of 7 psu. While peat in the unimpacted and restored sites were higher in elevation than the water level at low tide, the impacted site always had a few inches of water on it. We later found that the impacted site is back fed by the freshwater Nye Pond, and that the unimpacted and restored sites both receive some inputs from a neighboring cranberry bog.

Methods

Initial Collection and Analysis of Sediment Cores and Pore Water

We collected sediment cores from each of the three study sites in early November 2014. We cleared any litter from the collection site, and hammered plastic core tubes into the sediment with a mallet. We used a trowel to cut around the core tube to break any roots that prevented it from going in or out of the sediment. We took the duplicate cores in close proximity to one
another at each site. We sealed the bottoms of the core tubes with rubber stoppers for transport back to the lab. After the cores were removed from the sediment, I collected approximately 60mL of pore water from the remaining hole using a 60mL syringe with a stop cock and an attached tube of about 25cm in length.

Upon returning to lab, I filtered the pore water with GFF swinex filters and recorded the pH using a pH electrode and the salinity using a field refractometer. I then acidified approximately 10mL samples with 10µL 50% trace metal grade HCl and refrigerated them for later trace Fe analysis (Forstner 1980). We removed the sediment cores and cut them into 5cm sections using a serrated knife. We placed each section in an aluminum baking tray that had been cleaned with DI water and pre-massed, and obtained a wet weight before placing them in a drying oven set to 50°C for several days to dry. After recording the sections’ dry weight, I ground representative samples with a mortar and pestle and saved any remaining sample in a Ziploc bag.

From the ground samples, I took subsamples for exchangeable acidity and aluminum; easily oxidized iron; total iron; and total sulfur analysis. I obtained exchangeable acidity data and aluminum concentrations of each sample by first extracting 5g of sediment with 50mL 1N KCl, which I placed on a shaker table for 1hr and then let settle overnight. I then gravity filtered 25mL of the extracts and recorded the initial pH with continuous magnetic stirring. I added 4 drops of phenolphthalein solution to the sample and then titrated with 0.01M NaOH until the pH reached approximately 8.15, recording the volume of NaOH used. I then added 2.5mL of 1M KF to the sample and let stir for 30 minutes. If the pH after this time period had not dropped below 8.15, I titrated the sample with 0.01M HCl until the pH of 8.15 was reached, and recorded the volume of HCl used. The total amount of hydrogen protons in meq/g of each sample could then be calculated by multiplying the molarity of the NaOH by the volume used and then multiplying that product by the total volume of KCl extract, and finally correcting for the appropriate scale of units. The concentration of aluminum in the extracts could be calculated in the same manner, but with the HCl concentration and volume. In addition, percent acidity from aluminum could be calculated using the equation in Figure 2.

To obtain concentrations of easily oxidized Fe in the samples, I followed the procedure in Forstner 1980, but used only 15mL of 50% HCl for the digestion. The digestion did not take place in a water bath, and was allowed to sit overnight before dilution. To obtain total Fe
concentrations in the samples, I followed the Forstner 1980 procedure. I converted concentrations from the Atomic Absorption Spectrometer to \( \mu \text{mol/g} \) using the equation in Figure 3. I calculated the concentration of pyrite, FeS\(_2\), in the cores as the difference between the total iron and easily oxidized iron, and therefore did not report total iron results in this paper. I was also able to calculate the bulk density of the core sections by dividing the dry mass of the section by the volume of the section.

I obtained total sulfur content data by combusting approximately 0.2g sediment in a LECO S632 Sulfur Analyzer. Carbon content data was also obtained as supplementary data after analyzing the core sections for del\(^{13}\)C and del\(^{15}\)N. Carbonates in the sediments were removed in sediment samples prior to analysis via acidification (Foreman 2014). Isotope and nitrogen content information were not used in the context of my project.

Microcosm Experiment

We collected duplicate sediment cores from the impacted and unimpacted sites to perform a water addition microcosm experiment (Table 1). We collected cores in early November 2014, following the collection procedure described above. Cores were 30cm long, 7.62cm diameter PVC pipes. After collection, we sealed the bottom of the cores with plastic wrap held in place by rubber bands under a layer of aluminum foil held in place by duct tape until the cores could be transported back to the lab. We set the cores vertically in holders and closed their bottom ends with PVC caps sealed with silicone gel to prevent leakage. Holes in the center of the caps allowed water to flow out the bottom of the cores through tubing, and flow could be stopped by a stop cock. Scotch Brite sponges inside the bottom of the core acted as a filter for the water coming out, to prevent any sediment loss. I washed the cores with DI water before use, and the sponges soaked in a 1N H\(_2\)SO\(_4\) acid bath before use. We added the water treatments to the cores five times over a two week period, adding and draining about 100mL of water from the cores each time. We allowed the drained cores to drain more than 100mL of water, and adjusted some additions to ensure that each core was receiving and draining comparable amounts of water. We added DI water for the fresh water additions, and filtered 34psu seawater for the seawater additions. Any water sample that was left after I completed analysis was discarded in order to use the same collection containers for the next treatment.

I measured pH, alkalinity, salinity, and Fe content on the water that came out of the cores after each addition. Salinity, pH, and Fe content were measured in the same way as described
above for the initial pore water collection. I determined alkalinity by Gran titration. I titrated 5mL of sample at room temperature with 0.01N, 0.05N, or 0.1N HCl and continuous stirring until it reached a pH of 3.7. If the sample already had a pH less than 3.7, I assumed no alkalinity. I then added another increment of acid to decrease the pH by 0.1. I added this same volume of acid nine more times, recording the volume of acid added and the new pH with each step. I then calculated alkalinity, or acid neutralizing capacity (ANC), using the USGS online alkalinity calculator (Alkalinity 2013).

After the water addition treatments had concluded, we divided the cores into sections and followed the same solid phase analysis procedure as for the initial cores described above. This time, representative samples were ground using a Wig-le-bug and we did not analyze the experimental cores for carbon and nitrogen content, for isotope information, or for exchangeable acidity and aluminum content.

Tidal Flux

To obtain information about the water that was flowing into and out of each site with the rise and fall of the tide, we collected surface water samples throughout the day on November 16, 2014. High tide was at 8:30am. We collected 1L surface water samples from each of the three sites at 9:30 and 10:30am, when the tide was going out. Low tide was scheduled for 2:00pm, but when we took samples from the unimpacted site at 2:45 and from the impacted and restored sites at 4:00pm, the tide was still going out. Finally, we took a sample from the unimpacted site at 4:15pm when the tide began to rise again. No other samples were taken due to lack of time. I obtained the pH, salinity, alkalinity, and Fe content of these samples using the same methods for water analyses as described above.

Results

Initial Cores and Pore Water Analysis

For all solid phase parameters, the unimpacted and restored sites are similar with respect to their depth profiles. While the unimpacted site has a constant % carbon content through the depths of the cores, the profiles of the restored and impacted sites seem to be opposite, with the impacted site having a higher carbon content at the surface of the core (Figure 4). Profiles of iron oxides from cores in all three sites are similar, with the impacted site having a lower Fe oxide content at all depths (Figure 5). The magnitudes of sulfur in the cores from all sites are
reflected by the magnitudes of pyrite (Figures 6 and 7). The % sulfur content and pyrite concentration are much larger in the surface layers of the impacted site cores than in the restored and unimpacted sites. In addition, there is a large amount of error in the sulfur and therefore pyrite content in the impacted site between the duplicate cores, as shown only on the % sulfur graph below (Figure 6). There was very little error between the other sites’ cores, so error bars are not shown.

The pH and iron concentrations of the pore water collected after the initial cores were taken are similar across all sites, with only a slightly higher Fe concentration in the restored site (Table 2). In all initial cores, exchangeable acidity was low and no aluminum was found, so results are not reported in this paper.

Microcosm Experiment

Over the course of the experiment, the water that came out of both drained cores dropped in pH, as did the second fresh water addition core (Figure 8). The two seawater additions behaved similarly over the course of the experiment with respect to pore water pH, which remained somewhat constant (Figure 9). The total iron that came out of the cores was low except in drained core 2 and fresh water addition core 2 (Figure 10). All cores seemed to produce alkalinity, as the total alkalinity of the pore water was greater than the alkalinity of the fresh and seawater additions that were added. The seawater additions to cores from the unimpacted site generated the most alkalinity by far (Figure 11).

The solid phase chemistry of the cores did change in response to the microcosm experiment. In all treatments performed on cores from the impacted site, pyrite was oxidized. The opposite occurred in the two control cores from the unimpacted site, in which oxidized iron content decreased and pyrite was formed (Figures 12 and 13). In general, the total sulfur content of all cores remained constant and therefore did not change in response to the treatments (Figure 14).

Tidal Flux

Both the salinity and the alkalinity of the restored and impacted sites were low and similar throughout the day of the tide going out. The salinity and alkalinity of the unimpacted site were highest at high tide and when the tide began to come back in, and decreased as the tide went out (Figures 15 and 16). The iron concentrations of all tidal flux samples were low and results are therefore not reported in this paper.
Discussion

Initial Cores and Pore Water Analysis

Due to similarities in sediment chemistry depth profiles of the unimpacted and restored site cores, the restored site seems to have returned to its “original state”. This judgment is made under the assumption that the restored site had the same characteristics of the unimpacted site before it was restricted from tidal circulation. The difference of % carbon in the impacted and restored cores could reflect the plant types that thrive in salt and fresh water marshes (Figure 4). *Phragmites australis* is a plant that thrives in fresh water marshes and has a higher carbon content than salt water plants such as *Spartina alternaflora*. The sediment profiles could support that the impacted site was indeed similar to the unimpacted and restored sites at some point in time, as the bottom of the impacted site % carbon depth profile is the same as that of the unimpacted site today. The profile of the restored site could also indicate that it was indeed a fresher site at one time, with a higher % carbon content at the bottom of the profile which is similar to the magnitude at the surface of the impacted site today. These conclusions are only based on the % carbon profiles of the sediment cores collected. More information about the chemistry of the sediment and about the rates of sediment deposition and compaction in this marsh are needed to further support these conclusions.

The magnitude of sulfur in the surface layers of the impacted site reflects the observation that this is not a drained marsh. If this site was completely drained, iron would oxidize and there would be a much higher content of iron oxides than sulfur and pyrite in the impacted site. This is the opposite of what we found in these initial cores. We assumed that the site was flooded during our collection of the cores due to the freshwater pond feeding it from the back. However, this does not explain the magnitude of sulfur present in this site. It could be possible that the impacted site is actually flooded with seawater during extremely high tides or storm events through the small culvert below the railroad tracks. The dike could then have the opposite effect and trap the seawater in the impacted site. This theory is also supported by the fact that the surface water salinity at the impacted site is not completely fresh (Table 2). The magnitude and variability of the sulfur content of the impacted site could then be explained because incoming seawater is known to provide abundant $\text{SO}_4^{2-}$ to a salt marsh system (Biogeochemical 1997).
**Microcosm Experiment**

The three experimental treatments performed on cores from the impacted site intended to mimic the short term responses of that site to different degrees of diking and restoration. First, we added fresh water to two duplicate cores and allowed them to remain drained to mimic a marsh completely cut off from water flow. We then had a freshwater addition that was not drained. Given the information from the initial cores, this treatment may most accurately represent the impacted marsh at the East Sandwich Game Farm. We then added seawater to cores from the impacted site to mimic restoration. Finally, we took cores from the unimpacted site and added seawater to serve as a control for how a natural marsh would react to the conditions of this experiment.

Over the course of the experiment, I expected the pH in the drained cores to drop as the surface layers of the peat were aerated and the iron and sulfur oxidized. This causes the pH of the pore water to be reduced, as $\text{H}^+$ is produced in the oxidation reaction (Figure 17; Biogeochemical 1997). I did not, however, expect the pH to drop as it did in the second fresh water addition core, but this could be a result of the variable sulfur content of the impacted marsh. This core did have had a higher sulfur content at the end of the experiment than its duplicate, so oxidized sulfur could have been the cause of the unexpected drop in pH (Figure 14). The pH remaining constant in all seawater addition cores further reflects the idea that salt water systems buffer a drop in pH by adding sulfur into the system and preventing oxidation. This is a similar result to that found in a microcosm experiment of seawater additions to diked marsh cores by Portnoy and Giblin in 1997. In their experiment, pH first experienced a drop and then increased slightly to remain at a constant level similar to that of the seawater cores in this experiment (Biogeochemical 1997).

The two cores with the most iron that came out in the pore water in response to the treatments reflect those with a large drop in pH, further supporting the idea that iron was oxidized in these cores. The iron then leached out as the pore water pH was reduced.

Although the results indicate that alkalinity was produced in all the cores, the alkalinity generation in the freshwater addition cores was probably due to the history of the cores, not as a result of the experiment. Because the impacted site was not completely fresh and had some salt water content, that generation is probably just the residual salt water being flushed out. Because the control cores came from the unimpacted site, they produce the most alkalinity. Sea water
brings $\text{SO}_4^{2-}$ and other inorganic matter into salt marshes, and therefore increases the alkalinity, or the acid neutralizing capacity (Biogeochemical 1997).

If we assume that the cores used for the microcosm experiment started out similar in composition to the initial cores, they can be compared to the solid phase chemistry of the initial cores to determine how they changed in response to the experiment. In correlation with the reduced pH of the pore water in the cores from the impacted site, iron in the sediment was indeed oxidized and the pyrite concentration decreased. Further supporting the addition of sulfur and inorganic matter to the unimpacted salt marsh, oxidized iron present in the cores was reduced to pyrite, probably according to the reactions in Figures 18 and 19. There was no dramatic change in total sulfur in the cores in response to this experiment, so if any form of sulfur did react chemically this means it was probably retained as elemental sulfur in the cores.

**Tidal Flux**

The high salinity and alkalinity of the unimpacted site throughout the tidal flux supports the idea that seawater brings in a component to the salt marshes that buffer pH and generate alkalinity (Biogeochemical 1997).

**Conclusions**

Several conclusions can be drawn from the results of this project. First, it seems that the restored site at the East Sandwich Game Farm has indeed returned to conditions similar to those on the unimpacted, natural marsh. It is also evident that salt water systems generate more alkalinity than diked and fresh water marshes due to the introduction of sulfur and other inorganic matter to the marsh. From the short term water addition experiment, a dramatic drop in pH occurred in the drained fresh water cores. If a management conclusion can be drawn from this, it would be to restore salt marshes gradually to reintroduce the surrounding environment to tidal circulation and allow dependent flora and fauna to readapt. If I could have continued this project, I would have measured dissolved sulfate during the initial pore water collection and during the tidal flux collection to determine if the sulfur variability in the impacted marsh was indeed due to incoming seawater coming into the marsh and becoming trapped behind the culvert. I also would have measured sulfate in the pore water that came out of the cores during the microcosm experiment to obtain a better idea of the mass balance of the sulfur and iron in the cores in response to the experiment. The Long Creek Salt Marsh at the East Sandwich Game Farm in East Sandwich, MA is much more complex than we thought at the beginning of this
project. More historic information about the site is needed to characterize an unimpacted state of the impacted site today, as the combination of proximity to the fresh water Nye Pond and the larger distance from the ocean may reveal that the site was always characterized by a salinity gradient.

Acknowledgements

Thank you to Dr. Ken Foreman and everyone who made it possible for me to participate in the Semester in Environmental Science program. Thank you especially to Dr. Anne Giblin for her unwavering patience, guidance, and positivity throughout this independent project. Thank you to Sam Kelsey for assistance with the LECO S632 Sulfur Analyzer. Thank you to Arianna Cocallas and Katherine Klammer for their collaboration and teamwork. Thank you to the course TAs Rich McHorney, Fiona Jevon, Tyler Messerschmidt, and Nick Barrett for their advice and patience. Finally, thank you to Dr. Amanda Spivak for calling our attention to the East Sandwich Game Farm site and to Ed Houlihan and the Thornton W. Burgess Society for access.

Literature Cited


East Sandwich Game Farm. Thornton W. Burgess Society.

Foreman, Ken. Preparing, Packing, and Organizing CHN Samples. Semester in Environmental Science. Marine Biological Laboratory. 2014.


Figures and Tables

Figure 1. Aerial map of the three study sites along the Long Creek salt marsh. Cape Cod Bay is located at the top of the map. Arrows indicate the bridge and railroad that have impacted the marsh site behind them.

![Aerial map of the three study sites along the Long Creek salt marsh. Cape Cod Bay is located at the top of the map. Arrows indicate the bridge and railroad that have impacted the marsh site behind them.](image)

Figure 2. Calculating Percent Acidity from Aluminum in a sediment extract.

\[
\text{% Acidity form Al} = \left( \frac{\text{Concentration of Al}}{\text{Concentration of H}^+} \right) \times 100
\]

Figure 3. Calculating Total and Easily Oxidized Fe Concentrations from the Forstner 1980 digestion procedure.

\[
\left( \frac{\text{Concentration of Metal in mg/L} \times 0.1 \text{L Extract} \times \text{Dilution Factor}}{\text{Mass sediment in g}} \right) = \text{Concentration of Metal in } \mu\text{mol/g}
\]

Table 1. Tabular Description of Water Addition Microcosm Experiment.

<table>
<thead>
<tr>
<th>Cores Taken From:</th>
<th>Impacted</th>
<th>Impacted</th>
<th>Impacted</th>
<th>Unimpacted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental Treatment:</td>
<td>Fresh Water Added, Core Drained</td>
<td>Fresh Water Added</td>
<td>Sea Water Added</td>
<td>Sea Water Added</td>
</tr>
</tbody>
</table>


Figure 4. Depth Profiles of % Carbon in the initial cores.

Figure 5. Depth Profiles of Fe Oxides in the initial cores.
Figure 6. Depth Profiles of $\%$S in the initial cores.

Figure 7. Depth Profiles of FeS$_2$ in the initial cores.
Table 2. Initial Pore Water Characteristics.

<table>
<thead>
<tr>
<th>Site</th>
<th>Average pH</th>
<th>Salinity (psu)</th>
<th>Average Fe Concentration (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unimpacted</td>
<td>7.18</td>
<td>25</td>
<td>5.6</td>
</tr>
<tr>
<td>Restored</td>
<td>6.14</td>
<td>13</td>
<td>10.2</td>
</tr>
<tr>
<td>Impacted</td>
<td>6.04</td>
<td>7</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Figure 8. Change in Pore Water pH over the course of the Microcosm Experiment in the Fresh Water Additions and Drained Cores.
Figure 9. Change in Pore Water pH over the course of the Microcosm Experiment in the Seawater Additions and Control Cores.

Figure 10. Total Iron Concentrations of the Pore Water that Came Out of the Cores during the Microcosm Experiment.
Figure 11. Total Alkalinity Generated in the Pore Water that Came Out of the Cores during the Microcosm Experiment. The linear line represents the alkalinity of the fresh and seawater added to the cores during the experiment. Points to the right of the line indicate that alkalinity has been generated.

Figure 12. Total Solid Phase Iron Oxide Concentration in the Cores after the Microcosm Experiment.
Figure 13. Total Solid Phase Pyrite Concentration in the Cores after the Microcosm Experiment.

Figure 14. Total Solid Phase % Sulfur in the Cores after the Microcosm Experiment.
Figure 15. Salinity of the Tidal Flux over the Course of One Day. Lines indicate the outgoing tide, while the point sanding alone represents and incoming tide.

Figure 16. Alkalinity of the Tidal Flux over the Course of One Day. Lines indicate the outgoing tide, while the point sanding alone represents and incoming tide.

Figure 17. Oxidation of Pyrite FeS$_2$.

$$4\text{FeS}_2 + 14\text{O}_2 + 4\text{H}_2\text{O} \rightarrow 4\text{Fe}^{2+} + 8\text{SO}_4^{2-} + 8\text{H}^+$$
Figure 18. Reaction due to Reducing Conditions Produced by Seawater Flooding
\[ 2\text{CH}_2\text{O} + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^- \]

Figure 19. Reduction Reaction of Iron Oxides by Sulfide Generation
\[ 2\text{FeOOH} + 3\text{HS}^- \rightarrow 2\text{FeS} + \text{S} + 3\text{OH}^- + \text{H}_2\text{O} \]