

Subaqueous Disposal of Sulfidic Waste Rock:
Six-year laboratory batch experiment

June 2013

Minnesota Department of Natural Resources
Division of Lands and Minerals
500 Lafayette Road, Box 45
Saint Paul, MN 55155-4045

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Kim Lapakko
Lyn Leopold
Dave Antonson
Stephanie Theriault
Erin Mehleis

Minnesota Department of Natural Resources
Division of Lands and Minerals
500 Lafayette Road, Box 45
St. Paul, MN 55155-4045

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0. Executive Summary

Placing sulfide-bearing Minnesota mine wastes under water (subaqueous disposal) might provide a method of secure, permanent disposal by reducing the rate of sulfide mineral oxidation and the consequent release of acid and heavy metals. Addition of alkalinity or oxygen-consuming material might provide additional mitigative benefit. The project described below quantified reactions controlling release of acid and heavy metals from Minnesota rock for different subaqueous disposal strategies. Reactions at the rock-water interface suggested these releases would be initially reduced and indicated they would decrease with time.

Experiments were conducted for four to six years on Virginia Formation hornfels rock containing 12 - 14 weight percent pyrrhotite ($\text{Fe}_{0.9}\text{S}$). They evaluated the mitigative potential of 1) subaqueous disposal (238-week period of record); 2) subaqueous disposal augmented by addition of alkalinity to the water cover (230 weeks); and 3) incorporation of an oxygen consuming compost layer at the water/rock interface (324 weeks with leached solids from aforementioned experiment; 265 weeks with fresh solids). Thin layers of rock (~11 mm) were used to more precisely describe reactions at the water-rock interface.

Under subaerial conditions (562 weeks, simulating disposal on the land surface), rates of sulfide mineral oxidation increased by roughly a factor of five after 120 weeks of reaction. The initial rates were likely abiotic and the increase was attributed to microbial mediation of the reaction. Associated with this increase, pH decreased from the upper threes to near 3.0, and trace metals concentrations increased by as much as a factor of 30. Drainage pH values reached a minimum near 2.5 after about 200 weeks. After about 300 weeks of reaction, oxidation rates declined (and pH increased) due to depletion of 70 to 100 percent of the sulfide minerals initially present.

Initial sulfide oxidation rates from all subaqueous disposal conditions approximated initial subaerial rates, but oxidation rates did not increase as did the subaerial environment. In contrast, rates of sulfide mineral oxidation under unmodified subaqueous conditions declined by roughly 50 to 70 percent after 100 to 200 weeks of reaction. The decline was influenced by both sulfide mineral depletion and inhibition of oxygen transport due to iron oxyhydroxide precipitates. At this time 70 to 90 percent of the sulfide minerals present remained to oxidize at the slower rate. The minimum pH for subaqueous disposal with no modification was 3.3. Maximum release rates for copper, nickel, cobalt, and zinc from the subaqueous rock were 0.001 to 0.01 times those from the subaerial rock but did respond to pH changes in the water covers.

Removing residual soluble components from the rock surface prior to immersion, adding alkalinity to the overlying water during oxidation, and amending the waste rock (leached and fresh) with compost provided no further reduction in oxidation rates. Furthermore, the decline in oxidation rates in experiments using small additions of alkalinity or compost (3-4 mm) did not occur until 300 to 400 weeks of dissolution. This lag was roughly twice that for the unmodified subaqueous disposal. Both additions generally maintained circumneutral pH and, consequently, reduced copper, nickel, cobalt, and zinc release rates.

The results demonstrate the promise of subaqueous disposal and also infer cautions to be exercised. Because acid is contributed by both subaqueous iron sulfide mineral oxidation and residual acidic salts on the mine waste, these contributions must be quantified so that requirements to neutralize these inputs can be determined. Potential sources of neutralization include alkaline water inputs to the mine (e.g. with groundwater), dissolution of acid neutralizing minerals in the mine (e.g. mine walls, residual rock), and intentional addition of alkaline amendments.

1. Introduction

The Duluth Complex in northeastern Minnesota has been a target for mineral exploration since the mid-1960s. The Virginia Formation underlies the Duluth Complex and inclusions of this rock occur in the basal Duluth Complex (Severson and Hauck 1990, Geerts 1991, Severson 1993, Hauck et al. 1997). Concentrations of economic metals (e.g. copper, nickel, cobalt) in the Virginia Formation are low and most likely not economic. Consequently, Virginia formation rock excavated during mining of the Duluth Complex would likely be considered waste rock. Although the economic value of the Virginia Formation rock is low, it can contain substantial pyrrhotite (Severson and Hauck 1990, Geerts 1991, Severson 1993, Hauck et al. 1997).

When stored in contact with oxygen, pyrrhotite will oxidize to produce acid. As acid is generated, the pH of drainage or a water cover will decrease. Once the pH decreases below 4, biological mediation becomes predominant and accelerates the rate of sulfide mineral oxidation (Singer and Stumm 1970, Kleinmann et al. 1981, Nordstrom 1982). Pyrrhotite oxidation occurs through a series of steps by which iron is gradually removed from the crystal structure, often referred to as a shrinking core model (Nicholson and Scharer, 1994; Janzen 1996; Pratt et al., 1994a and b). At any point during oxidation, Fe^{2+} can be further oxidized to Fe^{3+} , which precipitates as an iron oxyhydroxide (e.g. FeOOH). As oxidation proceeds at the crystal surface, an iron oxyhydroxide layer forms. Iron-depleted, or alternately, sulfur-enriched intermediates form in layers between the oxide coating and unreacted pyrrhotite. Subsequent reaction requires iron to diffuse through these layers, decreasing the rate at which reaction occurs. Complete pyrrhotite oxidation can be described as follows.



The rate of pyrrhotite oxidation can be reduced if pyrrhotite-bearing rock is stored under water, for example in a mined-out pit. The main factor behind the success of subaqueous disposal of mine waste over that of surface disposal is the slow diffusion rate of oxygen in water, about 1/10,000 that in air. Presumably the addition of an oxygen-consuming layer above reactive mine wastes in a subaqueous environment would further slow oxidation rates. By reducing the rate of sulfide mineral oxidation, a reduction in rates of trace metal release would also be expected. Suppressing rates of acid and trace metal release can reduce impacts of these components on natural waters, thus subaqueous disposal presents a promising option for disposal of sulfidic mine wastes. Consequently, experiments were initiated to quantify rates of oxidation and trace metal release for rock in direct contact with the atmosphere (subaerial) and that for rock under water (subaqueous).

2. Objectives

In the present study the subaqueous oxidation of pyrrhotite ($\text{Fe}_{0.8-1}\text{S}$) present in mineralized Virginia Formation hornfels is examined. The water quality associated with this oxidation and the rates of oxidation under laboratory conditions are compared for subaerial (on-land) disposal and three variations of subaqueous disposal. The rates determined in conjunction with existing knowledge of oxygen transport are used to extrapolate the laboratory data to in-pit disposal in the field. Thin layers of rock were used in the subaqueous settings to allow examination of reactions occurring at the water-rock interface. In particular, this design permits examination of reactions over time that would be obscured in experiments on deeper rock beds.

The objectives this experiment were to describe the oxidation of sulfide minerals present in mineralized Virginia Formation rock and the associated trace metal release under the following conditions:

1. subaerial disposal environment in which the mine waste is subjected to wet-dry cycling,
2. subaqueous environment,
3. a modified subaqueous environment with regular alkaline addition to maintain circumneutral pH, and
4. subaqueous disposal amended with an oxygen-consuming compost layer.

The subaerial environment (objective 1) represents disposal of the waste rock on land, with periods of oxidation followed by flushing of oxidation products. The second objective (unmodified subaqueous disposal) represents the disposal of partly oxidized rock in an underwater environment, with no subsequent mitigation.

The third objective (modified subaqueous disposal with alkaline addition) simulated the addition of alkalinity in the form of a lime solution to the subaqueous disposal of both “untreated” and “pretreated” waste rock in two separate experiments. “Untreated” waste rock was simply the partly oxidized rock used in objectives 1 and 2 described above. Pretreatment of the waste rock was conducted by removing the metals and acid on the rock surface. These surficial solutes were largely generated by sulfide mineral oxidation while samples were stored after crushing and prior to experimentation. The pretreatment was investigated as a means of removing oxidation products from partly oxidized wastes in the field prior to subaqueous disposal. Throughout this presentation, the term “modified” will refer to the addition of alkalinity to the subaqueous environment.

The fourth objective (amended subaqueous disposal) simulated the addition of an oxygen-consuming layer above both leached and fresh waste rock. The use of a composted yard waste layer above rock may inhibit the depression of pH by providing alkalinity, impeding oxygen transport and serving as a substrate for sulfate-reducing bacteria. Throughout this presentation, the term “amended” will refer to the addition of this compost layer above the waste rock.

3. Background

Subaqueous disposal (submerged) has been gaining favor as a preferred option for sulfide-bearing mine waste disposal in Canada and Sweden (MEND, 1999; Natural Resources Canada; MiMi, 2001; SENES, 1995; and Tremblay and Hogan, 2001). Canada has an extensive mining industry, and the Canadian government has recognized the importance of limiting adverse environmental effects of the industry. MEND, the Canadian national research group on environmentally sound mine waste management, indicates that subaqueous disposal is the preferred option for unoxidized sulfidic mine wastes (Tremblay and Hogan 2001). Natural Resources Canada (2004) indicated their preferred hierarchy for waste rock disposal as, “(i) disposal in underground mines that eventually flood with water, (ii) disposal in mined-out pits which are completely filled with waste rock and till, and allowed to naturally saturate with groundwater, (iii) disposal in mined-out pits with a water cover of acceptable depth and chemical quality, and (iv) surface disposal of clean waste rock which is well segregated from special waste rock.” MiMi, a Swedish agency similar to MEND, indicated that the rate of sulfide mineral oxidation, which leads to release of acid and trace metals, is severely inhibited by subaqueous disposal (MiMi 2001).

A literature review was conducted to summarize current information on subaqueous disposal. Articles were chosen primarily from reports done through the Mitigation of the Environment Impact from Mining Waste (MIMI), International Conference on Acid Rock Drainage (ICARD), and Mine Environment Neutral Drainage (MEND) programs because they provide compilation of scientific articles on acid rock drainage. Articles that studied the subaqueous disposal of sulfide-bearing mine waste in anoxic environments, such as open pits or man-made lakes were the focus of this literature review. Additional information on data collection and analyses of trace metal and sulfate release, pyrrhotite or pyrite oxidation, and pH over long periods of time (years opposed to months) was of particular interest, as well. Laboratory studies were also reviewed for quantitative comparison and in field implications.

3.1. Case Studies of Subaqueous Disposal

The main factor behind the success of subaqueous disposal of mine waste (especially over that of surface disposal) is the slow diffusion rate of oxygen in water (almost 10,000 times slower than in water than in air). This therefore decreases the rate of sulfide oxidation dramatically. Also, there is about 25,000 times more oxygen in the air than there is in water (Barber et al., 1997). The Office of Surface Mining Reclamation and Enforcement (2000) noted that for subaqueous disposal to be effective, “a stagnant or no flow condition and relatively thick saturated zone appear critical. Stagnant flow conditions leading to the development of anoxic conditions and a saturated thickness on the order of several tens of feet appear to effectively curtail oxygen diffusion” (OSM, 2001).

The Flambeau Mine, Ladysmith, Wisconsin, United States

The Flambeau Mine is located near Ladysmith, WI and began operation as an open-pit copper-gold mine in July 1991. By the end of 1999, the open-pit mine was refilled with the waste rock, crushed limestone, and groundwater (WNDR, 2009). Water quality monitoring for pH, Cu, Fe, Mn, sulfate, and others began on a quarterly basis with the opening of the mine. After the pit was reclaimed, annual monitoring of Ba, Cd, Ca,

Cl, Cr, Pb, Mg, Hg, K, Se, Ag, Na, and Zn began in July 1999. In compliance with regulatory changes regarding arsenic in groundwaters, quarterly arsenic analyses began in 2005. Foth and Van Dyke and SRK Consulting conducted independent water quality testing and analysis for the Flambeau Mining Company, results from their analysis can be found in the most recent report, the Flambeau Mining Company 2009 Annual Report.

The Flambeau Mining Company 2009 Annual Report emphasizes that since 2000 the acidity in the backfill pore water has been neutralized by the limestone. Manganese concentrations have fluctuated between 40 and 80 µg/L, but are stable to slightly decreasing since 2007. Iron concentrations appear to be stable at low levels, and equilibrium modeling suggests that iron levels are controlled by saturation with respect to iron oxyhydroxides. Similarly, sulfate levels are believed to be controlled by gypsum saturation, except in isolated areas of groundwater inflow, where sulfate concentrations are low. A long-term increasing trend in for copper was identified, however copper concentrations decreased during 2009. Long-term trends for Ba, Cd, Ca, Cl, Cr, Pb, Mg, Hg, K, Se, Si, Na and Zn were not considered to be statistically significant. The report concludes that concentrations of solutes in the backfill pore water are stable and the flux of pore water from the backfill will be negligible with respect to its potential impact on water quality in the Flambeau River” (Flambeau Mining Company, 2009). Thus, the reclamation of the Flambeau Mine is on its way to becoming a successful example of the subaqueous disposal of sulfide-bearing mine waste.

Owl Creek and Collins “B”, Ontario, Canada

Various studies on mine waste disposal were done through SENES and MEND in the late 1980’s through early 1990’s. Two case studies involving the subaqueous disposal of waste rock are Owl Creek and Collins “B.” Both indicate that subaqueous disposal of waste rock is successful in slowing sulfate release.

Owl Creek is an old gold mine located northeast of Timmins, Ontario. As of 1989 about 4,770,000 metric tons of waste rock had been taken out of the mine and were either used in road construction, a diversion channel for the Porcupine River, or deposited in one of three dumpsites. In 1990, scientists found that ARD had been migrating into the Porcupine River from the dumpsites lowering the pH to about 2.3. Elevated concentrations of Zn, Cu, Ni, Fe, and Al were also found in the river. In order to mitigate the problem, they decided to dispose of the waste rock with crushed limestone additions into the Owl Creek open pit and allow natural flooding to occur. They chose this option for four reasons: “The option provided a walk-away type decommissioning plan for the reactive waste rock, the generation of additional acid would be inhibited and it was likely that the existing acidity released in the pit would be neutralized, the open pit had the capacity to contain the waste rock, and the plan could be implemented sooner and at an overall lower cost” (SENES, 1995). The neutralization of the acid within the pit would be a result of limestone additions previous to deposition within the pit.

After implementation of the pit disposal, the water quality was tested on a monthly basis both by the company and the Ontario Ministry of Environment and Energy (MOEE). Data collected shows that the pH leveled out between 7.9 and 6.6 from its initial pH of about 2.3 and the overall water quality is improving. The success of this operation was due to the acidic pore water neutralization from limestone additions, the quick flooding, the storage capacity beneath the water table, and the water table’s natural elevation (SENES, 1995).

Uranium mining ceased at Collin's "B" in 1991. After the decommissioning of the mine, the pit was subsequently filled with $4.3 \times 10^5 \text{ m}^3$ of waste rock and then allowed to flood. Since decommissioning, Cameco continues to monitor the in-pit disposal site, collecting data on the surface quality and groundwater quality. Surface water quality was determined through the analysis of temperature, dissolved oxygen, conductivity, pH, and redox. Concentrations were also taken for trace metals, radionuclides, nutrients, and other major constituents. Groundwater quality was monitored through assessing the movement of the constituents with piezometers, which indicated that there was little movement of constituents from the waste rock in the pit through the water. Principle findings suggest that water quality is improving with time, but arsenic and nickel levels were higher than the standards outlined by the government (SENES, 1995).

Solbec Tailings Pond, Quebec, Canada

Amyot and Vézina studied data from the Solbec tailings pond between 1972 and 1980 and subsequent testing from 1995 to 1998 to try and determine how mine waste (specifically tailings) reacts in a subaqueous environment. Earlier studies submitted by the Ministry of Environment and Wildlife in 1985 suggested that AMD was ongoing and subsequent flooding was needed to mitigate the problem. Between 1990 and 1993 the MEND program devised a feasibility plan for the flooding the tailings pond. Work began in 1994, with flooding and water testing started in 1995. Monitoring for pH and heavy metal concentrations (specifically Fe, Zn, and Cu) continued through 2011 (Blier and Amyot 2012).

In general the pH values fluctuated during the initial stages of work and flooding, but it eventually leveled out at neutral. In the upper-most layer of water (cover water) concentrations of iron, copper, and zinc all stabilized at low levels by spring 1995. Both iron and copper concentrations in all water layers gradually decreased with minimal to no anomalous changes. Zinc concentrations increased rapidly during the flooding event. Blier and Amyot (2012) reported that after 15 years, the water cover has met all requirements set by the Quebec Environmental and Wildlife Department, with copper and zinc levels below 0.1 mg/L and circumneutral pH.

Pennsylvania Underground Coalmine, United States

Donovan et al. (2003) analyzed data collected from a Pennsylvanian underground coalmine that was backfilled with sulfur rich coal deposit waste rock and then groundwater flooded it. Mining began in 1958 and ceased in 1980, which is when the backfilling and flooding began, allowing for substantial oxidation of the mining waste to occur. Subsequent water quality tests were done to confirm that the subaqueous disposal of waste rock reduced or eliminated ARD. Alkalinity, pH, and concentrations of Fe, Al, Mn, Ca, Mg, Na, K, SO_4 , and Cl were all studied. Data was collected on a weekly to monthly basis for 18 years between 1983 and 1999.

Donovan et al. (2003) found that the water chemistry experienced three phases over the 18 years of data recovery. Phase I consisted of a declining pH characterized by high acidity and iron concentrations. This phase lasted from year 0 to year 2. Phase II was considered the "transition" between phases I and III and it was characterized by declining iron concentrations. This phase was observed between years 2 and 4. Phase III remained constant throughout the rest of the data collection, consisting of a late increase in pH and the gradual decline in the concentration of the

remaining constituents including iron and acidity. In general, a “transition from net-acidic to net-alkaline conditions” within the water column was documented (Donovan et al., 2003).

One of the most important conclusions Donovan et al. reached is with extensive ore-flooding oxidation that “The ramifications of this phenomenon are that long-term fluxes of iron and metals, as well as general water chemistry, may not be adequately predicted from observations of mine-water chemistry either *in situ*, prior to flooding, or *ex situ* in pumped overflow from flooded mines, after such flooding is complete. It may take years—perhaps greater than a decade, depending on mine-specific factors—before the evolution of mine water chemistry has stabilized and approached the long-term values of pH, iron and major ion chemistry that will prevail over many years following mine closure” (Donovan et al., 2003).

Elliot Lake, Ontario, Canada

At the Elliot Lake mine in Ontario, partially oxidized Uranium tailings containing 5 to 10% pyrite were mixed with lime and deposited into pits, which were then allowed to fill with rainwater, runoff, and infiltration, shallowly covering the tailings-limestone mixture to slow oxidation of the sulfide minerals. Over the 12 years of pit operation, subsequent limestone additions were implemented to maintain a neutral pH within the pit. The amount of limestone additions were recorded and used to determine the acid generation rate through time. Ludgate et al. found that through time the amount of limestone addition has decreased therefore suggesting that acid generation by the oxidation of sulfide minerals is decreasing as a result of limestone additions to subaqueous disposal (Ludgate et al. 2003, Nicholson et al. 2012).

Eskay Creek

Morin and Hutt (2000) studied a mine waste disposal site that was relocated twice due to issues with ARD. Initially the tailings were disposed on land, but the ARD became an issue and subsequent planning for a subaqueous dumpsite was implemented. To determine if the ARD issue was under control, measurements of pH, neutralization potential (NP), concentrations of Zn, Pb, Cu, Ni, Ca, Co, Fe, Ar, Cd, and Sb, specific conductance, alkalinity, and bulk rate of oxidations were made.

In 1990, the tailings were deposited into the valley site for subaqueous disposal and groundwater, runoff, and the Eskay Creek were allowed to flow in. However during the following winter pH levels were around 3, suggesting the subaqueous method was not working in this area, perhaps due to the movement of water via the creek. It was then decided to relocate the tailings into a nearby “biological-barren alpine lake.” After the first year of relocation into the alpine lake the pH leveled out at 4.7 with zinc and lead concentrations of about 5 and 0.2 mg/L respectively; after three years the pH increased to near neutral values and the zinc and lead concentrations fell to about 0.2 and 0.009 mg/L, respectively. Morin and Hutt (2000) concluded that “The relocation of the acid-generating waste rock to an underwater location provided a net-benefit to the environment...this lowered environmental liabilities and long-term treatment costs by (1) placing the rock underwater where its drainage no longer required treatment...and (2) restoring the water quality of the watershed where the dump was once located to near-background levels within three years.”

Fox Lake, Sherridon, Manitoba, Canada

Moncur et al. (2012) examined the long term results of submerged pyrite- and pyrrhotite-rich tailings from the Sherritt-Gordon Cu-Zn mine into Fox Lake, near Sherridon, Manitoba. Tailings were deposited in the lake at the end of mining in 1951, and sampled in 2009. Solid-phase analyses of the submerged tailings indicated an oxidation zone of only a few centimeters compared to 40 to 60 cm in the land-based tailings. Pore water chemistry within the submerged tailings was compared to both land-based tailings and Fox Lake water. Sulfate concentrations were consistently in the range of 100 mg/L and circumneutral pH in both the submerged tailings pore water and in Fox Lake, compared to approximately 7500 mg/L sulfate and pH between 1.9 and 4.6 in the land-based tailings pore waters. Most dissolved metals (Fe, Zn and Cu reported) were at or below detection limits in the submerged tailings pore water (Moncur et al. 2012).

3.2. Laboratory Tests on Subaqueous Disposal

Laboratory column leaching studies were done through the MEND program in 1998 to determine the “acid generation characteristics and subsequent metal and radionuclide release” of samples disposed either in subsurface or subaqueous sites (MEND 1998a). The experiments were conducted for about four years. It was found that underwater disposal decreased the overall acidity of water and sulfate and iron loadings significantly in comparison to subsurface disposal.

Lysimeter studies were also done to determine the “surface oxidation, leaching and mass release characteristics” for subaqueous disposal of unoxidized tailings (that have been previously underwater for more than 12 years) and partially oxidized tailings (MEND 1998b). During the study, the unoxidized tailings slowly began to oxidize and at the water-tailings interface acidity, Mn, and Pb concentrations were low, and Ca, Mg, and Ra-226 concentrations were high in comparison to the surface water (MEND 1998b). The rates of oxidation for the partially oxidized tailings were also very slow, however high amounts of acidity and metal concentrations were found at the tailings-water interface, but diffusion to the surface was moderate to low. For both cases, it was found that “the slow oxidation of underwater deposited tailings at the surface as well as the dissolution and release of metals and radionuclides from the oxidized surface have been important factors in determining the surface water quality” (MEND 1998b).

Davé and Paktunc (2003) examined the differences between subaqueous disposal of tailings in fresh and saline water. Tailings were collected from the Tilt Cove subaqueous tailings site, the fresh water came from a natural lake near Ottawa, and the saline water came from Tilt Cove. Data was collected for pH, acidity, and dissolved concentrations of sulfate, calcium, iron, aluminum, copper, and zinc about every month for 1.5 years in both the surface and pore waters. In general, for all the pore and surface water for both saline and fresh water conditions the metal concentrations and the acidity show an increasing trend and the decreasing trend for pH through time. The sulfide mineral oxidation rate for the fresh water cover was more than six times that for the saline water cover. Davé and Paktunc (2003) attributed this to the additional alkalinity within the saline water cover that delayed the acidification. It is important to note, therefore, that if the cover water for mine waste exhibits some degree of alkalinity, the initial rate of oxidation of sulfide minerals will be further inhibited.

Studies performed by Davé et al. (1997) were done to determine the “oxygen diffusion, oxidation, leaching, and ion/metal release/flux characteristics” of waste rock and tailings during subaqueous disposal. The waste rock was partially oxidized and weathered from the Mine Doyan, Lac Minerals, Val d’or, Quebec

with a sulfur content of about 4%. Two different tests were conducted; one to determine the oxygen diffusion and the other to determine oxidation and leaching characteristics. The oxygen diffusion tests were conducted for 61 days with data collection on days 0, 1, 7, 29, and 60 for dissolved oxygen concentrations at different depths. The oxidation and leaching characteristics data was collected about 1 year after the water cover was introduced for pH, total acidity, dissolved iron, and dissolved aluminum at different depths.

Results for the oxygen diffusion test and the oxidation and leaching test for the partially oxidized waste rock found that underwater disposal does not entirely stop nor prevent oxidation, rather it is reduced to low levels, the amount of water above the waste does not affect oxygen diffusion, oxidation, or leaching if the subaqueous conditions remain constant, municipal compost or low sulfur tailings covers act as oxygen consuming layers inhibiting any oxygen to come into contact with the tailings, and the subaqueous disposal of waste rock led to low concentrations of acidity, sulfate, and metals (Davé et al., 1997).

Morin (1993) studied the rates of sulfide oxidation in subaqueous environments where he concluded that sulfide oxidation rates are much slower in subaqueous environments. As mentioned above, this is due to the lack of oxygen. Morin also thought it is imperative to note that “However, a sometimes-overlooked observation is that oxidation will still occur whenever gaseous/dissolved oxygen reaches submerged sulfide minerals. Since water exposed to the atmosphere can carry approximately 10 mg/L of dissolved oxygen, then at least some oxidation can be expected whenever oxygenated water flows through saturated sulfide-bearing tailings or mine rock” and that “site specific conditions dominate in determining the eventual water chemistry” (Morin, 1993). These relationships along with the variability of water chemistry show how important it is for scientists and companies to understand the chemistry of the subaqueous environment before disposal.

Laboratory leaching tests on pyritic tailings (7.2 weight percent) from the Elliot Lake Quirke mine done by Paktunc and Davé (2003) were to determine the changes and controls on pyrite oxidation rates over time. Tests were conducted for 7.5 years and data was collected weekly from the drainage effluent to determine the pH, Eh, electrical conductance, the total acidity and alkalinity, and dissolved SO₄, major metals, and radionuclides concentrations. Oxidation rates were calculated by determining the amount of pyrite dissolution through time. The tests concluded, “The mean rates below pH 1.5 are 2.78×10^{-10} mol (m² pyrite·s)⁻¹ and 2.60×10^{-10} mol (m² pyrite·s)⁻¹ for 10 µm particles. The rates above pH 1.5 and below neutral pH values vary as a function of pH,” (Paktunc and Davé 2003). The rates for pH values between 1.5 and 3.5 were comparable to reported oxidation rates at a pH of 2. This is significant because for the reported pH 2 rates oxygen was the only oxidant, suggesting that in this experiment oxygen was the only force acting as an oxidizing agent. Therefore, similar field oxidation rates would also suggest that oxygen is the only oxidizing agent.

Yanful and Simms (1996) reviewed a series of field and laboratory methods in determining the feasibility of subaqueous tailings disposal. One study involved examining three cases of waste disposal, which varied through water and lime additions, concluding that “The use of a water cover greatly improved water quality” (Yanful and Simms, 1996). Another study they reviewed was the Solbec Cupra field trials. These trials were done to determine the effects of disposing the Solbec Cupra tailings underwater with limestone additions. Redox potential, pH, and concentrations of iron, calcium, potassium, magnesium, sulfate, lead, and zinc were measured for both the surface water and pore water. Additionally, electrical conductivity, dissolved oxygen, alkalinity were measured for the surface water.

For the cover waters, pH ranged from neutral to pH ~8, dissolved oxygen content ranged from 6-17 mg/L, iron was less than 0.5 mg/L. Calcium, potassium, magnesium, copper, chromium, mercury, argon, and nickel were all at low concentrations in both the cover and supply water, suggesting the tailings had no effect on these metals. Lead and zinc levels were higher in the cover water than in the supply water, but in general they were low. Sulfate concentrations were more than 10 times higher than the supply water (Yanful and Simms, 1996).

The pore waters pH increased as you go down through the tailings. Yanful and Simms (1996) suggest that this is due to the “tailings large buffering capacity.” Heavy metal concentrations decreased with depth beneath the pit basin. Copper, zinc, and iron concentrations tended to be higher than the rest and sulfate concentrations were higher in the oxidized tailings. Yanful and Simms (1996) suggest the high sulfate concentrations in the water cover and oxidized tailings were caused by the dissolution of gypsum.

In general for the surface water “with the exception of the low pH measurements observed at the beginning of seasons, all measured parameters were below effluent discharge standards” (Yanful and Simms, 1996). They also concluded that lime additions reduced the rates of release for metals, except for zinc.

In general, laboratory observations by Yanful and Simms (1996) found that if lime is added to the tailings, the pH subsequently increases and the mobility of some metals into both surface and pore waters is limited. It should also be noted that it could be more effective to mix the lime with the top layer of tailings than to just add lime to the surface. Therefore based on both laboratory observations and field studies, Yanful and Simms (1996) concluded that the ARD can be reduced significantly “more than any other known methods” with the application of a water cover, sand layers reduce metal fluxes and act as a protective cover. Also, protective covers act as an oxygen and resuspension barrier, therefore reducing oxidation of the tailings.

4. Methods

4.1. Solid Phase Materials and Analysis

4.1.1. Virginia Formation Hornfels Waste Rock

The rock used in the experiment was mineralized Virginia Formation hornfels that was collected, crushed, and wet-sieved in March 1989. The plus 270-minus 100-mesh fraction ($0.053 < \text{particle diameter} \leq 0.149$ mm) was retained for experimental use and stored in plastic bags until the inception of this experiment in September 1990.

Sulfur contents, as determined by LECO furnace, of the two samples used in the study were 5.13% and 5.96%, respectively. Acid digestion (U.S. Bureau of Mines 1980) and digestate analysis by atomic absorption spectrophotometry (Perkin Elmer 603) indicated that over 97 % of the sulfur was associated with iron (Table 1). X-ray diffraction and electron microscopy (SEM/EDS) of a heavy mineral concentrate indicated the presence of both hexagonal ($\text{Fe}_{0.9}\text{S}$) and monoclinic ($\text{Fe}_{0.875}\text{S}$) (Mattson 1994). The pyrrhotite content of the samples was calculated based on the chemical analyses, assuming all sulfur not associated with trace metals was present as hexagonal pyrrhotite. It should be noted, however, that later it was determined that the pyrrhotite was about 75 percent monoclinic and 25 percent hexagonal (average stoichiometry = $\text{Fe}_{0.88}\text{S}$) (Mattson 1994). For the purposes of this report, any difference in these stoichiometric calculations was assumed to be negligible. Alteration shells, most likely iron oxides, were observed on the pyrrhotite grains, suggesting that slower oxidation rates would be expected (Figure 1). The presence of these alteration shells on unleached particles is unexpected. Copper was assumed to be present in equal amounts of chalcopyrite and cubanite (CuFeS_2 and CuFe_2S_3), and nickel was assumed to be present as pentlandite [$(\text{Fe}, \text{Ni})_9\text{S}_8$]. Cobalt and zinc were assumed to be present as simple sulfides (i.e. CoS , ZnS).

Transmitted light microscopy of a similar mineralized VFH sample (Graber 1990) indicated the rock contained 32% quartz, 32% opaques (sulfides, oxides, and graphite), and 19% of a clay mineral, probably kaolinite. Feldspar and chlorite each contributed 5%, and phlogopite and muscovite each contributed 4%.

Table 1. Sulfur, trace metal, and pyrrhotite content of mineralized Virginia Formation hornfels samples. (All values in wt %.)

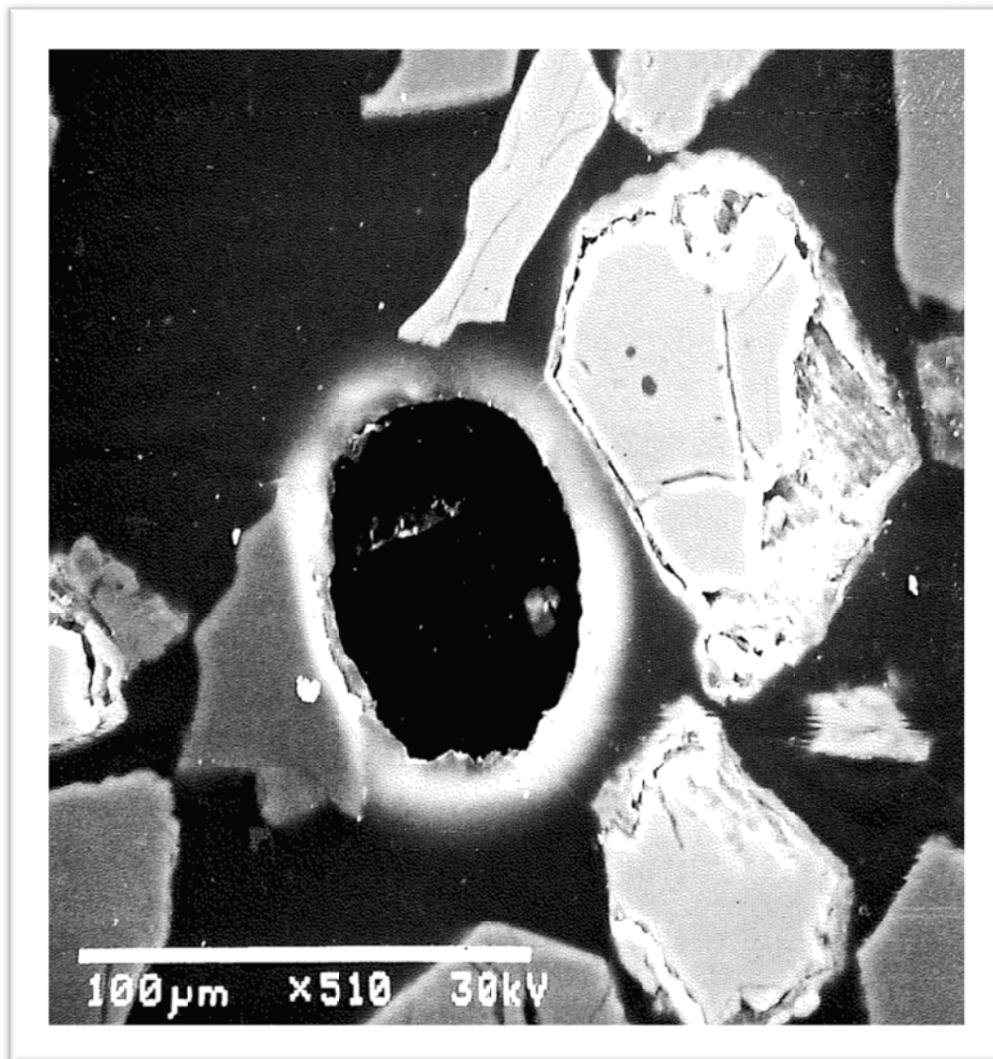
Sample	S	Fe	Cu	Ni	Co	Zn	Pyrrhotite
A ¹	5.13	6.3	0.11	0.052	0.011	0.083	12.8
B ²	5.96	7.25 ³	0.14 ³	0.068 ³	0.012 ³	0.084 ³	14.9

¹ Used for subaerial, unmodified subaqueous, and subaqueous with alkaline addition simulation.

² Used for pretreated subaqueous with alkaline addition.

³ Average of analyses of duplicate samples.

Figure 1. Alteration shells, most likely iron oxyhydroxides, were observed on unleached pyrrhotite mineral grains from Virginia hornfels waste rock used in the subaqueous flask experiments. SEM photo of polished surface with grains from Sa. #10392 superpanner concentrate. The pyrrhotite grains (lightest gray) all exhibit an alteration shell. Note the small dark gray silicate inclusions in large pyrrhotite to right of black center void. Small flame inclusions of pentlandite were noted in several grains. Chalcopyrite (elongate light gray above void) and pyrite (medium gray, top edge) are also shown. The darker gray grains are various oxides and silicates. 510X magnification, scale bar represents 100 microns.



4.1.2. Composted Yard Waste

The yard waste was initially deposited at a Hennepin County (Hassan Township) drop-off site, composted for about 180 days, and shipped to Recomp (St. Cloud Transfer and Recycle) in St. Cloud, Minnesota, where it was screened to -1/2 inch. The yard waste was composted in an open pile which was monitored for temperature and moisture and watered and turned regularly. It was received from Recomp in a 50-lb plastic bag, a subsample of which was stored at room temperature in a sealed five-gallon plastic pail. Duplicate samples of bulk compost were analyzed at the U.S. Bureau of Mines in Pittsburgh for percent water, ash, calcium, magnesium, sodium, potassium, and sulfate, as well as sulfate, copper, nickel, and zinc contents. The percentages of organic nitrogen, ammonia nitrogen, nitrate nitrogen, total phosphorous, and sulfate along with lead, chromium, and cadmium contents were determined at the University of Minnesota.

At the end of March 1995 the compost was sieved to separate the -6/+8 mesh fraction (2.38 – 3.36 mm diameter), part of which was retained for experimental use and the remainder was placed into a freezer bag for storage. At this time the moisture content was determined to be 30.8%, based on analysis of triplicate samples (Table E4).

To determine the potential of the compost to neutralize acid, two grams of moist compost were placed in a small beaker to which 10 mL of distilled water was added. The sample was placed on a stirrer and titrated with 0.02 N sulfuric acid to pH endpoints 6.0, 5.0 and 4.5. A Ross combination pH electrode (8165) and an Orion 720A pH meter were used to determine pH. The endpoints were determined when the pH remained stable for at least 30 seconds. Three determinations were made for the 6.0 and 4.5 endpoints. Two determinations were made for the 5.0 endpoint. The average neutralization potentials for endpoint pH values of 6.0, 5.0, and 4.5 were 0.45, 6.5, and 10.4 mg/g CaCO₃.

4.2. Aqueous Phase Analyses

An Orion SA 720 pH meter with a Ross combination pH electrode (8165) was used for pH analysis, and a Myron L conductivity meter was used to determine specific conductance. Alkalinity and acidity were analyzed using standard titration techniques (APHA et al. 1992). Sulfate was analyzed using an HF Scientific DRT-100 nephelometer for the barium sulfate turbidimetric method (APHA et al. 1992). Calcium, magnesium, copper, nickel, cobalt, and zinc were analyzed at the MN DNR Minerals Office in Hibbing using a Perkin Elmer 603 atomic absorption spectrophotometer in the flame mode through week 185 for flasks 1 - 6 and week 171 for flasks 7 and 8. Subsequent analyses were determined at the Minnesota Department of Agriculture. Metals were determined with a Varian 400 SPECTRAA; a Zeeman GFAA furnace was attached for low concentrations. Sulfate concentrations were determined using a Technicon AA2 automated colorimeter or, for [SO₄] <5 mg/L, a Dionex ion chromatograph. The reaction conditions and approximate sampling schedule are presented in Table 2.

Table 2. Description of aqueous phase sampling methods and schedule for the initial set of laboratory subaqueous disposal experiments.

Unit	Experimental Objectives	Sample frequency	Sample Volume (mL)	Notes
Period of Record = 238 weeks				
1,2	Subaerial disposal simulation		175	Rinsed weekly with 200 mL
3,4	Unmodified subaqueous disposal		25 100	Withdrawn sample volume replaced with distilled water
5,6	Modified subaqueous disposal of untreated rock with alkaline addition	weekly- SC ¹ , pH monthly- SO ₄ , Ca, Mg, trace metals	25 100	Withdrawn sample volume replaced with distilled water
7,8	Modified subaqueous disposal of pre-treated rock, with alkaline addition		25 100	Withdrawn sample volume replaced with distilled water
Period of Record = an additional 324 weeks				
1, 2	Subaerial, continued		175	Rinsed weekly with 200 mL
4, 6, 8	Subaqueous control, continued, no additional alkalinity	weekly- SC, pH monthly- SO ₄ , Ca, Mg, trace metals ²	25 100	Withdrawn sample volume replaced with distilled water
3, 5, 7	Amended subaqueous with compost layer, leached solids		25 100	Withdrawn sample volume replaced with distilled water
Period of Record = 20 for compost controls, 265 weeks for 11-14				
9, 10	Compost controls	Variable ³ :	25 100	Withdrawn sample volume replaced with distilled water
11, 12	Subaqueous control with fresh solids	every 4 to 8 weeks- SC, pH;		
13, 14	Amended (compost) subaqueous with fresh solids	every 1 to 3 months- SO ₄ , Ca, Mg, trace metals ⁴	25 100	Withdrawn sample volume replaced with distilled water

¹SC = specific conductance

²Trace metals were not measured between weeks 92 and 210; after week 210 measurements were between 1 and 3 months.

³Measurements were made weekly between weeks 1-21, bi-monthly between weeks 21-144, and monthly between weeks 144-265.

⁴Trace metals were not measured between weeks 34 and 148.

4.3. Dissolution Procedures

Four experimental objectives were studied in separate phases over a period of eleven years (Table 3):

1. Subaerial disposal environment,
2. subaqueous environment,
3. subaqueous environment modified by alkaline addition, and
4. subaqueous disposal amended with compost.

The initial phase of experiments investigated waste rock disposal in a subaerial environment (Objective 1), an unmodified submerged environment (Objective 2), a modified submerged environment with regular alkaline addition (Objective 3), and a modified submerged environment with regular alkaline addition after removal of oxidation products from the rock surfaces (Objective 3). Dissolution continued for a period of 238 weeks for this initial phase of experiments, with the exception of the pretreated rock which was started later and ran for 224 weeks. At the conclusion of this initial phase, all alkalinity addition ceased.

The second phase of study was a continuation of the initial subaqueous experiments. A layer of composted yard waste was added on top of the waste rock in one duplicate of each of the previous subaqueous conditions and the record was reset to week one (Objective 4). The other duplicate was continued as a control. Dissolution under these amended conditions continued for 324 weeks. A third phase, compost addition to fresh waste rock, was initiated separately from the earlier experiments, and continued for 265 weeks (Objective 4).

Table 3. The period of record for each of the initial laboratory subaqueous disposal experiments varies from 20 to 324 weeks. “Modified” refers to the addition of alkalinity to maintain circumneutral pH. “Amended” refers to the addition of a compost layer.

Experimental Objective	Description	Unit Numbers	Start Date	End Date	Period of Record (weeks)
1	Subaerial (on-land) disposal	1, 2	9/12/1990	4/5/1995	238
2	Unmodified subaqueous	3, 4	9/12/1990	4/5/1995	238
3	Modified subaqueous with alkaline addition	5, 6	9/12/1990	4/5/1995	238
3	Modified subaqueous with alkaline addition, pretreated rock	7, 8	12/19/1990	4/5/1995	224
4	Amended subaqueous with compost layer	3, 5, 7	4/5/1995	6/19/2001	324
4	Compost controls, subaqueous	9, 10	5/22/1996	4/10/1996	20
2	Fresh waste rock controls, subaqueous	11, 12	5/22/1996	6/19/2001	265
4	Amended subaqueous with compost layer, fresh solids	13, 14	5/22/1996	6/19/2001	265

4.3.1 Subaerial Disposal Simulation (Objective 1)

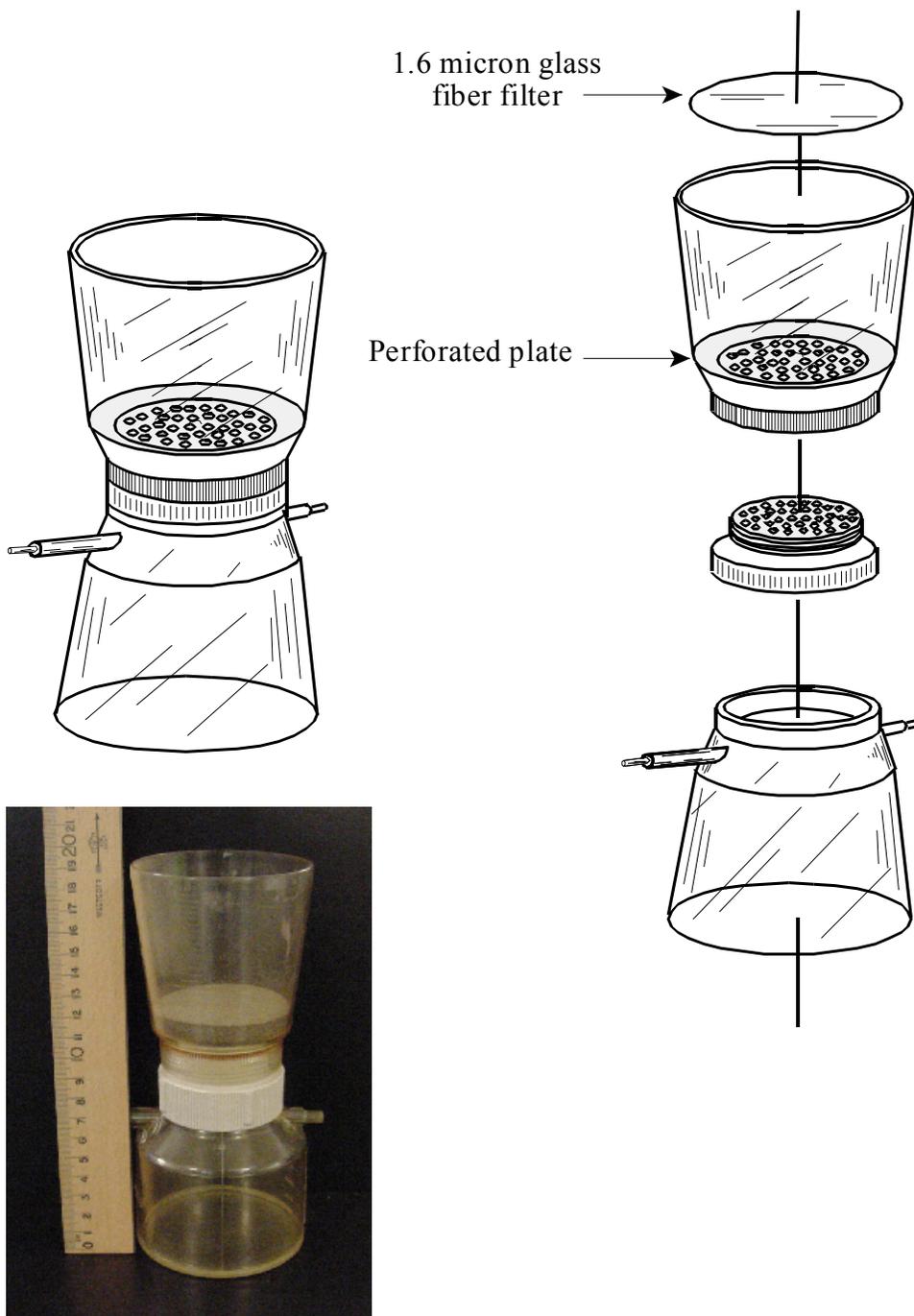
To simulate subaerial disposal, duplicate 75-g samples were placed onto a perforated plastic plate (covered by a glass fiber filter) in the upper segment, or reactor, of a two-stage filter unit (reactors 1 and 2; Figure 2). Prior to the inception of the experiment, the reactor was placed onto the lower segment (receiving flask) of the unit, upon which was placed a 0.45- μm filter. Samples were then rinsed with three distilled water volumes of 200 mL, to remove products that accumulated from oxidation during sample storage. To each reactor, 200 mL of distilled water was added and allowed to stand for 5 min; it was then drawn by vacuum through the mine waste sample and 0.45- μm filter into the receiving flask. The average drainage volume of water obtained from rinsing the solids was 175 mL.

Between rinses the solids were retained in the reactors to oxidize further and stored in individual compartments of a wooden housing. A thermostatically controlled heating pad was placed beneath the housing to control temperature. The reactors were stored in a small room equipped with an automatic humidifier and dehumidifier, to maintain a stable range of humidity. Temperature and relative humidity were monitored two to three times a week. The average weekly temperature ranged from 20.5° to 28.7° C, with an average of 24.7° C and a standard deviation of 1.58 (n=237). The relative humidity ranged from 38% to 76%, with an average of 54.2%, and a standard deviation of 5.12% (Table E2).

The volume of rinse water, or drainage, was determined by weighing the receiving flask. Solution pH was analyzed directly in the lower stage of the reactor, and aliquots were withdrawn for on-site determinations of specific conductance and acidity or alkalinity. Samples were also taken for subsequent analysis of metals and sulfate. Samples taken for metal analyses were acidified with 0.2 mL AR Select nitric acid (Mallinckrodt) per 50 mL sample.

It is important to note that several laboratory errors were detailed in the lab notes for these two reactors over the initial 116 weeks (Appendix E1). Around week 22, at least one of the subaerial reactors was accidentally tipped over. Spilled solids were recovered and returned to the reactors. However, subsequent data analysis indicated excessive sulfate release unit 2. Both units 1 and 2 were massed, and it was determined that spilled solids from unit 1 were probably placed incorrectly in unit 2. However the mass of this error could not be determined with any certainty. Thus, mass release calculations (specifically sulfur) must be considered as approximate values.

Figure 2. Schematic and photo of small reactor



4.3.2. Subaqueous Disposal and Modified Subaqueous Disposal (Objectives 2 and 3)

The initial phase of subaqueous disposal conditions, both with and without alkaline addition modifications, were all examined in duplicate (Table 4). In each case 200 g of waste rock and 1.8 liters of distilled water were added to a 2-L Erlenmeyer flask (Figure 3). The depth of solids was relatively thin, estimated to be 7 mm. However, visual examination of the flasks suggested solid depths of up to 11 mm in some places. Glass wool was placed in the mouth of the flask to retard evaporation while allowing oxygen transport into the flask. The flasks were stored in the same controlled temperature and humidity room as the wet-dry cycle reactors.

The pH of the solution was measured directly by inserting the electrode into the flask. Monthly 100-mL samples were withdrawn from a depth of about 8.3 cm in the flasks, which had an average water depth of 13 cm, for determination of specific conductance and alkalinity or acidity. The remaining sample was filtered (0.45 μm) for subsequent determination of sulfate, calcium, magnesium, copper, nickel, cobalt, and zinc. Samples taken for metal analyses were acidified with 0.2 mL AR Select nitric acid (Mallinckrodt) per 50-mL sample. On weeks that sulfate and metals were not sampled pH was determined directly in the flasks, and a 25-mL sample was removed for specific conductance and alkalinity or acidity analyses. Distilled water was then added to replace the volume lost to sampling and evaporation and, thereby, maintain a constant water volume within the apparatus.

For the subaqueous disposal environment (units 3 and 4), untreated rock was placed into the flasks with no further modification. “Modified subaqueous disposal” objectives were examined using both untreated and pretreated rock. For the first, “modified subaqueous disposal” environment (units 5 and 6), untreated rock was placed into the flasks, and an alkaline solution (hydrated lime dissolved in distilled water) was added when the pH dropped below 7.25. The alkalinity of this solution typically ranged from 1,400 to 2,000 mg/L as CaCO_3 . For the second, “modified subaqueous disposal” environment (units 7 and 8), the 200-g rock samples were first rinsed with approximately 5.7 liters of distilled water to remove acid and other products generated by weathering. The samples were next rinsed with 4.1 liters of a solution of hydrated lime and distilled water (average alkalinity 1,030 mg/L as CaCO_3). A subsequent rinsing with 6.4 L of a solution of sulfuric acid and distilled water (average acidity 310 mg/L as CaCO_3) because the alkaline solution rinses produced a pH in excess of 11 on the rock sample surface. In total, each sample was subjected to 151 rinses of 100 to 120 mL. For the final rinse, 100 mL of distilled water was passed through the solids bed, and the pH of the effluent was between 7.6 and 7.8.

Table 4. Summary of the experimental designs and objectives for the initial phase of subaqueous disposal experiments (238 weeks).

Description	Units	Experimental Objective
Subaqueous disposal	3, 4	2
Modified subaqueous disposal with alkaline addition using untreated rock	5, 6	3
Modified subaqueous disposal with alkaline addition using pretreated rock	7, 8	3

Figure 3. Subaqueous disposal simulations were conducted in 2-L Erlenmeyer flasks. This picture was taken in August 2012, after completion of the experiment. Duplicate pairs of experimental conditions are shown side by side. Compost amendments were added to the odd-numbered units (on the left) of each duplicate in the second phase of experiments after 238 weeks of dissolution.



4.3.3. Subaqueous Disposal of Leached Solids Amended with Compost (Objective 4)

At the conclusion of the initial phase subaqueous disposal experiments (week 238), all alkalinity addition ceased and the composted yard waste amendments began. The period of record for the second phase was reset to week 1 once the compost was added to each flask. Three 75-gram (wet weight) samples of +10 mesh composted yard waste were split out using the four corners method and added to the odd-numbered flask from each of the three duplicate pairs (Figure 4, Table 5). It should be noted that due to a pH decrease in unit 7, an additional 75-g layer of yard compost was added to this unit on week 58. This second addition of yard compost was added in such a way as to cover visually determined patches of exposed tailings.

Dissolution of waste rock in the even-numbered duplicates from the first phase of subaqueous and modified subaqueous experiments continued as controls with no further alkaline additions. Weekly sample volumes were removed and analyzed using the same methods as described for the initial subaqueous experiments.

During the initial phase of subaqueous experiments, net calcium consumption led to the question of saturation with respect to gypsum in the water covers. Gypsum precipitation would also remove sulfate, decreasing apparent sulfate release rates. Consequently, it was decided to replace the water covers with distilled water in order to better quantify the rate of sulfate release by reducing the potential for gypsum precipitation. On week 262, the water covers were siphoned off until a depth of approximately 3/4 to 1 inch remained. The water covers were replaced with distilled water, added using a separatory funnel and Tygon tubing without disturbing the solids remaining in the flask. This procedure was repeated on week 271.

Table 5. Summary of the experimental designs used for the second phase of subaqueous disposal experiments amended with composted yard waste (324 weeks beginning at compost addition).

Description	Units	Experimental Objective
Subaqueous disposal controls	4, 6, 8	2
Subaqueous disposal amended with composted yard waste	3, 5, 7	4

Figure 4. Compost amendments (75-g) were added to each of the odd-numbered (left) subaqueous leached waste rock simulation duplicates. Even-numbered units served as controls.



4.3.3. Subaqueous Disposal of Fresh Solids Amended with Composted Yard Waste (Objective 4)

The previous experimental design used Virginia hornfels rock that had been leached for approximately four and a half years to evaluate the effect of compost addition. To measure the effect of compost on the release rate of sulfate from the oxidation of pyrrhotite in fresh Virginia hornfels, six four-liter beakers were used (Table 6). The first pair, called compost controls, contained 75 grams of composted yard waste with 3.6 liters of water cover. The second pair, the waste rock controls, held 200 grams of mineralized Virginia Formation hornfels (5% S) and 3.6 liters of water cover. Two hundred grams of waste rock were covered with 75 grams of yard compost and then 3.6 liters of water were placed in the third pair. Weekly sample volumes were removed and analyzed using the same methods as described for the initial subaqueous experiments.

In the previous set of subaqueous experiments, net calcium consumption led to the question of saturation with respect to gypsum in the water covers. Gypsum precipitation would also remove sulfate, decreasing apparent sulfate release rates. Consequently, it was decided to replace the water covers with distilled water in order to better quantify the rate of sulfate release by reducing the potential for gypsum precipitation. On week 209, the water cover was siphoned off until a depth of approximately 3/4 to 1 inch remained. The water cover was replaced with distilled water, added using a separatory funnel and Tygon® tubing without disturbing the solids remaining in the flask. This procedure was repeated on week 213.

Table 6. Summary of the experimental designs used for the third phase of subaqueous disposal experiments: fresh waste rock amended with composted yard waste. (Period of Record = 265 weeks).

Description	Units	Experimental Objective
Compost controls	9, 10	Na ¹
Waste rock controls	11, 12	2
Subaqueous disposal amended with composted yard waste ²	13, 14	4

¹Compost control experiments were used to determine water quality due to the compost alone and did not directly test any of the experimental conditions set out in the objectives.

²Also referred to as “combination hornfels and compost” in some older files.

4.4. Release Rate Calculation Methods

Sulfate, calcium and magnesium release rates were calculated for all three phases of subaqueous disposal experiments in order to evaluate each of the four experiment objectives (subaerial, subaqueous, subaqueous modified by alkaline addition and subaqueous amended with compost). Copper, cobalt, nickel and zinc release rates were calculated for the first phase of subaqueous disposal experiments only.

Cumulative mass release for specific solutes were determined by adding the mass of solute removed by sampling plus the mass estimated to remain in the reaction vessel. Solute cumulative mass release was then plotted over time and periods of linear mass release were determined by visual inspection. Solute release rates were calculated using linear regression for each visually determined period of linear mass release, where the slope represents release in mmol/week. These values were then normalized to the mass of rock used in each reaction unit and converted to $\text{nmol} (\text{kg rock} \cdot \text{s})^{-1}$.

5. Results

5.1. Subaerial Disposal Simulation (Objective 1, Units 1 & 2)

Subaerial disposal drainages clearly indicated that the rock was a fairly strong acid producer. The results presented in this section focus on the first 238 weeks of the total record (562 weeks). This period was selected to coincide with that for the initial phase of the subaqueous flask experiment. The drainages from the duplicate reactors exhibited similar temporal variations in quality (Figure 5). Drainage pH was near 4 for about 100 weeks, declined rapidly to near 3 where it remained for about thirty weeks, then slowly declined to fairly steady values between 2.5 and 2.8 until week 300. The duplicates deviated in the timing of the pH declines, however, beginning at weeks 109 and 137 for unit 1 and weeks 93 and 129 for unit 2. Thus, the temporal pH trends in the duplicates were similar, but there was roughly a fifteen-week difference in the timing of the pH declines. While the discrepancy cannot be fully explained, lab notes indicated issues with filtration throughout the first 116 weeks of the experiment, and these problems might have contributed to the differences (Appendix Table E1). Subsequent to week 300, the drainage pH began to gradually increase, reaching approximately 5.5 by week 560 and the end of the period of record.

Concentrations of sulfate and other solutes were high at the beginning of the experiment and decreased until about week 10, reflecting the release of oxidation products that accumulated before the inception of the experiment. For all experimental conditions, the amount of sulfate on the rock surfaces ranged from 5 to 8 mg per gram rock. Since this initial “rinse-off” period did not quantitatively address rates of sulfide mineral oxidation, it is generally ignored subsequent discussions. The aqueous sulfate release observed subsequently was attributed to sulfide mineral oxidation.

Whereas pH replicated well and demonstrated continuous trends in units 1 and 2, sulfate and other solute concentrations tended to be a bit more erratic. Between weeks 12 and roughly 100, sulfate concentrations typically fluctuated between 40 to 65 mg/L (Figure 5). However around week 100, concurrent with the rapid pH decrease, sulfate concentrations increased to roughly 200 mg/L. A second rapid increase in sulfate levels to nearly 400 mg/L occurred at about week 200, which coincided with the pH reaching a plateau at 2.5. Sulfate levels fluctuated in the range of 250 – 400 mg/L until week 300, and then declined rapidly to the range of 25 – 35 mg/L. At 400 weeks, sulfate levels decreased slowly, reaching 3 mg/L by week 562. Cumulative sulfate release calculations indicated that after 300 weeks of dissolution, approximately 75% (65 and 90% for duplicates) of the sulfide minerals in the waste rock were depleted (see section 4.3.1). Sulfate release rates during weeks 12 to 100 averaged $2.0 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ (Table 7). After roughly week 100, the average sulfate release rate increased to $9.5 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, coinciding with the observed elevation in sulfate concentrations and the rapid decrease in pH (Table 7).

Calcium concentrations generally fluctuated within the range of 2 to 5 mg/L and calcium release rates were steady at roughly $0.3 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ through 238 weeks, (Figure 5 and Table 7, respectively). Subsequent to week 238, calcium levels began to gradually decrease, reaching less than 1 mg/L by week 320, and 0.1 mg/L by the end of the period of record at week 562.

Magnesium concentrations increased rapidly from less than 5 mg/L during the initial 100 weeks to fluctuating levels around 10 mg/L and spikes as high as 25 mg/L after week 100 (Figure 5). The period of elevated magnesium concentrations persisted until roughly week 260, when magnesium levels began to

decline. By week 400, magnesium levels had reached 1 mg/L and continued to decrease to approximately 0.2 mg/L by the end of the period of record at week 562. This trend was similar to that observed for sulfate concentrations and similarly, corresponded to the pH decrease around week 100 (Figure 5). Again, similar to sulfate, magnesium release rates averaged $0.5 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ for approximately 100 weeks, but increased to $1.8 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ as the pH decreased to 2.5 (Table 7). These results were consistent with what would be expected due to the pH-dependent dissolution of magnesium-bearing silicate minerals present in the rock (e.g. phlogopite, chlorite). However, the solid phase analyses were not sufficient to provide additional insight as to what mineral phases might be involved.

Of the four trace metals examined, copper and zinc exhibited a response to the decrease in pH (Figure 5). Copper concentrations increased from near zero over the first 100 weeks to a peak of 2-3.5 mg/L around week 200, leveled off around 1.5 mg/L until week 305, and subsequently decreased to less than 0.02 mg/L at the end of the 562 week period of record. Following a similar pattern, copper release rates increased from $0.002 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ prior to the pH decrease to an average of $0.08 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ after (Table 8). Zinc showed a similar trend, increasing from 0.5 to 2-3.5 mg/L, falling back to the 0.5 mg/L range by week 217, and decreasing to approximately 0.02 mg/L by week 562 (Figure 5). Zinc release rates were initially higher than copper, at $0.01 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ and increased to $0.08 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ as pH decreased (Table 8). However after approximately 210 weeks, zinc release rates dropped back to $0.02 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$. By the end of the experiment, cumulative mass release calculations indicated that roughly 35% of the copper and 45% of the zinc in the waste rock was depleted.

The highest concentrations for nickel and cobalt occurred at the beginning of the experiment during the rinsing off of oxidation products. These levels continued a downward trend toward detection limit values ($<0.01 \text{ mg/L}$) throughout the experiment (Figure 5). Release rates for nickel and cobalt were initially 0.1 and $0.01 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, respectively, and gradually decreased over the period of record reaching 0.007 and $0.003 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, respectively after 158 weeks (Table 8). Inspection of the cumulative mass release of these metals indicated that roughly 95% of nickel and 50% of cobalt present in the rock had been depleted.

Figure 5. Drainage quality results from the subaerial waste rock disposal simulations (Units 1 & 2). A sharp decrease in pH is marked by a corresponding increase in sulfate, copper and zinc at approximately week 100.

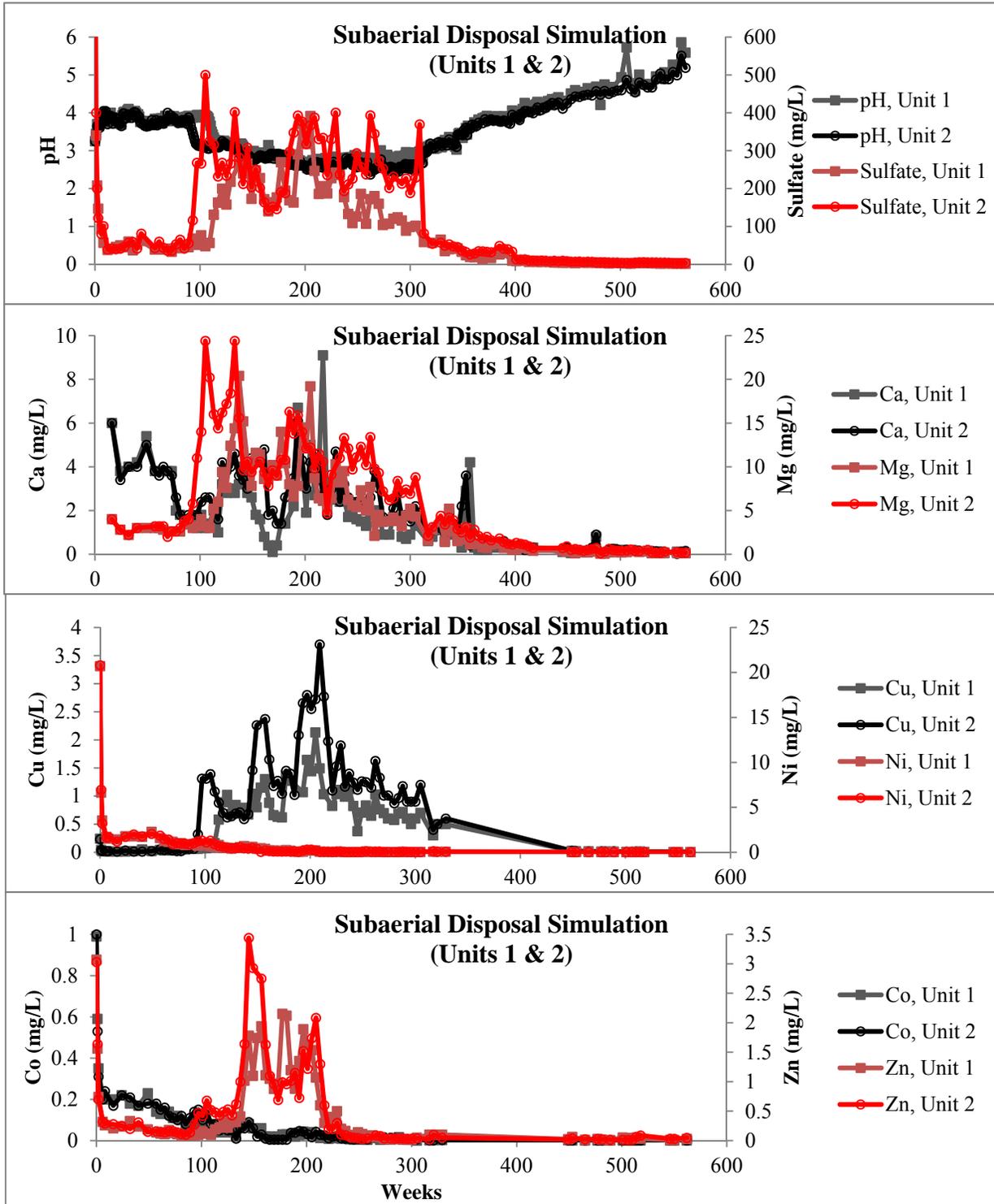


Table 7. Release rates [$\text{nmol (kg rock}\cdot\text{s)}^{-1}$] for the subaerial disposal simulation (Unit 1 & 2). Increased sulfate release rates after roughly 100 weeks was concurrent with pH decreasing below 3.0 and likely biologically mediated. Calcium release rates remained steady throughout the period of record, while magnesium release rates increased concurrent the decrease in drainage pH around week 100.

Release Rates $\text{nmol (kg rock}\cdot\text{s)}^{-1}$									
Parameter	Unit 1				Unit 2				Average
	Rate Period (weeks)	Rate	R ²	N ¹	Rate Period (weeks)	Rate	R ²	N ¹	
Sulfate	0-11	4.2	0.95	6	0-11	4.4	0.97	6	4.3
	12-109	1.9	1.00	23	12-93	2.1	1.00	19	2.0
	109-238	8.9	1.00	32	93-238	10.1	1.00	37	9.5
Calcium	12-109	0.3	0.98	19	12-93	0.4	1.00	15	0.4
	109-238	0.2	0.98	32	93-238	0.3	1.00	37	0.3
Magnesium	12-109	0.5	1.00	19	12-109	0.5	1.00	15	0.5
	109-238	1.6	1.00	32	109-238	1.9	0.99	37	1.8

¹N represents the number of measured concentration values. Regression calculations used estimated values (average of previous and post measured values) to fill in weeks when samples were not taken.

Table 8. Trace metal release rates [nmol (kg rock·s)-1] for the subaerial disposal simulations (Units 1 & 2).

Trace Metal	Unit	Period (weeks)	Rate	R ²	N	N ¹ (below d.l.)
Cu	1	12-106	0.002	0.98	18	0
		106-238	0.06	0.99	33	0
	2	12-91	0.002	0.97	14	0
		91-238	0.09	0.99	37	0
Ni	1	12-60	0.1	1.00	6	0
		60-158	0.04	0.99	25	0
		158-238	0.007	1.00	20	4
	2	12-60	0.1	1.00	6	0
		60-158	0.05	0.98	25	0
		158-238	0.007	1.00	20	4
Co	1	12-60	0.01	1.00	6	0
		60-158	0.004	0.99	25	0
		158-238	0.003	0.97	20	0
	2	12-60	0.01	1.00	6	0
		60-158	0.006	0.99	25	0
Zn	1	12-136	0.01	0.99	26	0
		138-208	0.08	1.00	17	0
		208-238	0.02	0.99	8	0
	2	12-91	0.01	0.99	14	0
		91-212	0.07	0.98	30	0
		212-238	0.02	0.94	7	0

¹ In these experiments, trace metal concentrations were frequently below detection limits, and therefore estimated at half the detection limit. In these cases, trace metal release rates should be considered an upper bound for release and are designated with “<” in the table.

5.2. Subaqueous Disposal (Objective 2, Units 3 & 4)

For subaqueous disposal condition with no further modification or amendments, replication was very good. In both cases pH declined steadily from 4.5 initially to a value of 3.5 after 120 weeks (Figure 6). Subsequently pH declined more slowly, reaching 3.3 at the end of the experiment (238 weeks). Initial sulfate concentrations were about 450 mg/L (Figure 6). These elevated concentrations and the initial low pH reflected the release of acidic reaction products that had accumulated on the rock owing to oxidation prior to the experiment. During the initial 36 weeks sulfate concentrations decreased from roughly 450 to 250 mg/L, where they remained for eight weeks. From week 44 to 65, sulfate concentrations increased to approximately 350 mg/L, where they remained until week 125. Subsequently, sulfate concentrations gradually decreased, reaching 170 mg/L by the end of the 238-week period of record (Figure 6).

Ignoring the initial “rinse off” period, sulfate release rates for the unmodified, unamended subaqueous condition remained constant at $1.3 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ for 205 weeks (Table 9). Subsequently, sulfate release rates decreased sharply to $0.3 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, reflecting the decline in sulfate concentrations. Cumulative mass release at the end of the record (week 238) indicates that only 11% of the available sulfur was depleted, suggesting that some mechanism must be inhibiting oxidation of the remaining sulfide minerals.

Calcium concentrations decreased throughout the experiment from initial concentrations of approximately 20 mg/L to less than 10 mg/L by week 238. Magnesium showed a similar trend with initial concentrations in the range of 50 – 65 mg/L decreasing to 25 – 30 mg/L by week 238 (Figure 6). Calcium and magnesium release rates averaged 0.1 and 0.7 $\text{nmol (kg rock}\cdot\text{s)}^{-1}$, respectively, and remained constant throughout the period of record (Table 9). Concentrations decreased despite the calcium and magnesium release because the rate of cation removal during sampling exceeded their respective rates of release during mineral dissolution. The water volume removed during sampling was replaced by distilled water, consequently diluting concentrations in the flask (section 4.3.2).

Trace metal concentrations and release rates were substantially lower in the subaqueous disposal simulation compared to the subaerial simulation. Copper concentrations increased from near zero in the initial phase to a peak of 0.2 – 0.3 mg/L, roughly an order of magnitude less than the subaerial disposal experiments (Figure 6). Similarly, copper release rates were also lower than in the subaerial simulation (Table 10). Copper release rates over the initial 146 weeks of the experiment averaged $0.0003 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, and increased to an average of $0.001 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ subsequently. Zinc concentrations increased to a peak of approximately 1 mg/L during the first 93 weeks, and remained in the range of 0.6 – 1.0 mg/L for the duration of the experiment (Figure 6). Furthermore, zinc release rates were the highest of the four trace metals measured, averaging $0.005 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ over the 238 week period of record (Table 10).

The highest concentrations for nickel, and cobalt occurred at the beginning of the experiment during the rinsing off of oxidation products (Figure 6). Subsequently, nickel and cobalt levels continued a downward trend toward below detection limit values ($<0.01 \text{ mg/L}$) throughout the experiment. Nickel release rates were low, averaging $0.0004 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ (Table 10). Calculated cobalt release rates were extremely low at $0.00006 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$. However, cobalt release rate should be considered an upper bound to potential cobalt release under these conditions due to the fact that roughly one third of the cobalt concentrations were below detection limits and were estimated as half the detection limit. Cumulative mass release calculations indicated that less than 7% of these trace metals were released into solution.

Figure 6. Sulfate, calcium, magnesium, nickel and cobalt concentrations, as well as pH, generally decreased over time in the subaqueous waste rock disposal simulations (Units 3 & 4). Copper and zinc concentrations increased to approximately 0.4 and 1 mg/L, respectively.

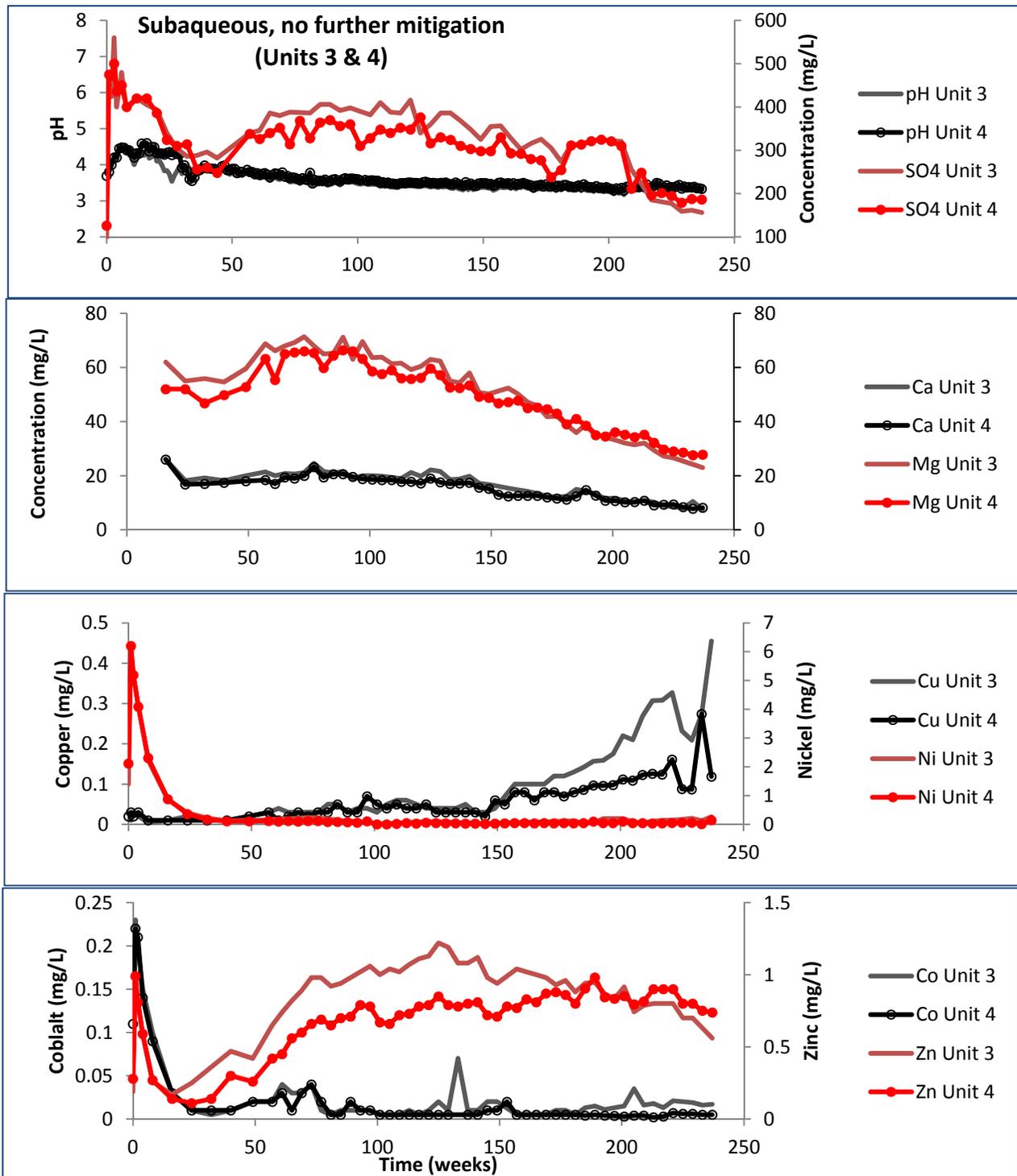


Table 9. Release rates [nmol (kg rock·s)⁻¹] for the subaqueous disposal simulation (Unit 3 & 4). Decreased sulfate release after 206 weeks was likely due to formation of coatings on the mineral surface.

Release Rates nmol (kg rock·s) ⁻¹							
Parameter	Rate Period (weeks)	Unit 3		Unit 4		N ¹	Average
		Rate	R ²	Rate	R ²		
Sulfate	0-23	3.1	0.85	3.0	0.86	10	3.0
	24-205	1.4	0.99	1.2	1.00	44	1.3
	206-238	0.1	0.39	0.4	0.91	8	0.3
Calcium	24-238	0.1	0.98	0.1	0.98	49	0.1
Magnesium	24-238	0.7	0.97	0.7	0.98	49	0.7

¹N represents the number of measured concentration values. Regression calculations used estimated values (average of previous and post measured values) to fill in weeks when samples were not taken.

Table 10. Trace metal release rates [nmol (kg rock·s)⁻¹] for the subaqueous disposal simulations (Units 3 & 4).

Trace Metal	Unit	Period (weeks)	Rate	R ²	N	N ¹ (below d.l.)
Cu	3	24-146	0.0003	0.98	26	0
		146-238	0.002	0.97	22	0
	4	24-141	0.0002	0.97	25	0
		141-238	0.0008	0.97	23	0
Ni	3	24-238	0.0006	0.91	48	3
	4	24-238	0.0002	0.89	48	7
Co	3	24-238	< 0.00009	0.91	48	11
	4	24-238	< 0.00004	0.80	48	19
Zn	3	24-238	0.006	0.99	48	0
	4	24-238	0.005	1.00	48	0

¹ In these experiments, trace metal concentrations were frequently below detection limits, and therefore estimated at half the detection limit. In these cases, trace metal release rates should be considered an upper bound for release and are designated with “<” in the table.

5.3. Subaqueous Disposal of Untreated Rock, Modified by Alkaline Addition (Objective 3, Units 5 & 6)

Replication was very good for the duplicate flasks simulating subaqueous disposal of untreated rock with alkaline addition. The pH of water in the two flasks was maintained in the typical range of 6.7 to 7.5, and it must be noted that pH was adjusted to maintain circumneutral conditions as part of the experimental procedure. Sulfate concentrations followed the same trend observed for the unmodified subaqueous disposal. Concentrations decreased from about 520 to 300 mg/L during the first 40 weeks and subsequently increased to around 400 mg/L (Figure 7). After the initial seven weeks sulfate release was steady at an average of $1.7 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ (Table 11).

The addition of alkalinity in the form of a hydrated lime solution elevated calcium concentrations in the modified subaqueous test units. Calcium concentrations decreased quickly from 140 mg/L to approximately 80 mg/L during the first 40 weeks, then increased to about 145 mg/L at about week 125 (Figure 7). Subsequent calcium levels fluctuated between 130 - 150 mg/L. Taking into account the amount of calcium added to the system due to the alkaline additions, negative release rates indicated a net removal of calcium from solution at approximately $-0.3 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ (Table 11).

Magnesium levels decreased throughout the experiment from initial concentrations of approximately 50 mg/L to roughly 13 mg/L by week 238 (Figure 7). Magnesium release rates averaged $+0.3 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ (Table 11). Concentrations decreased despite the calcium and magnesium release because the rate of cation removal during sampling exceeded their respective rates of release during mineral dissolution. The water volume removed during sampling was replaced by distilled water, consequently diluting concentrations in the flask (section 4.3.2).

Copper concentrations remained low, near 0.01 mg/L, throughout the experiment. The highest concentrations for nickel, cobalt, and zinc occurred at the beginning of the experiment during the rinsing off of oxidation products. Concentrations declined over time and decreased to levels typically below detection (generally $< 0.01 \text{ mg/L}$) after 101 weeks (Figure 7).

Trace metal release rates were extremely low, on the order of $10^{-5} \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ with the exception of nickel ($0.0003 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$) (Table 12). However these rates, excluding those of zinc after week 97, were calculated from estimated concentrations in place of measured values that fell below detection limits. Therefore, these release rates should be considered an upper limit rather than absolute values. Cumulative mass release calculations indicated that less than 3% of these trace metals were released into solution.

Figure 7. In the modified subaqueous disposal of untreated waste rock simulations (Units 5 & 6), circumneutral pH was maintained by adding alkalinity. Sulfate concentrations fluctuated around 400 mg/L, while trace metal concentrations were low, generally at or below detection limits.

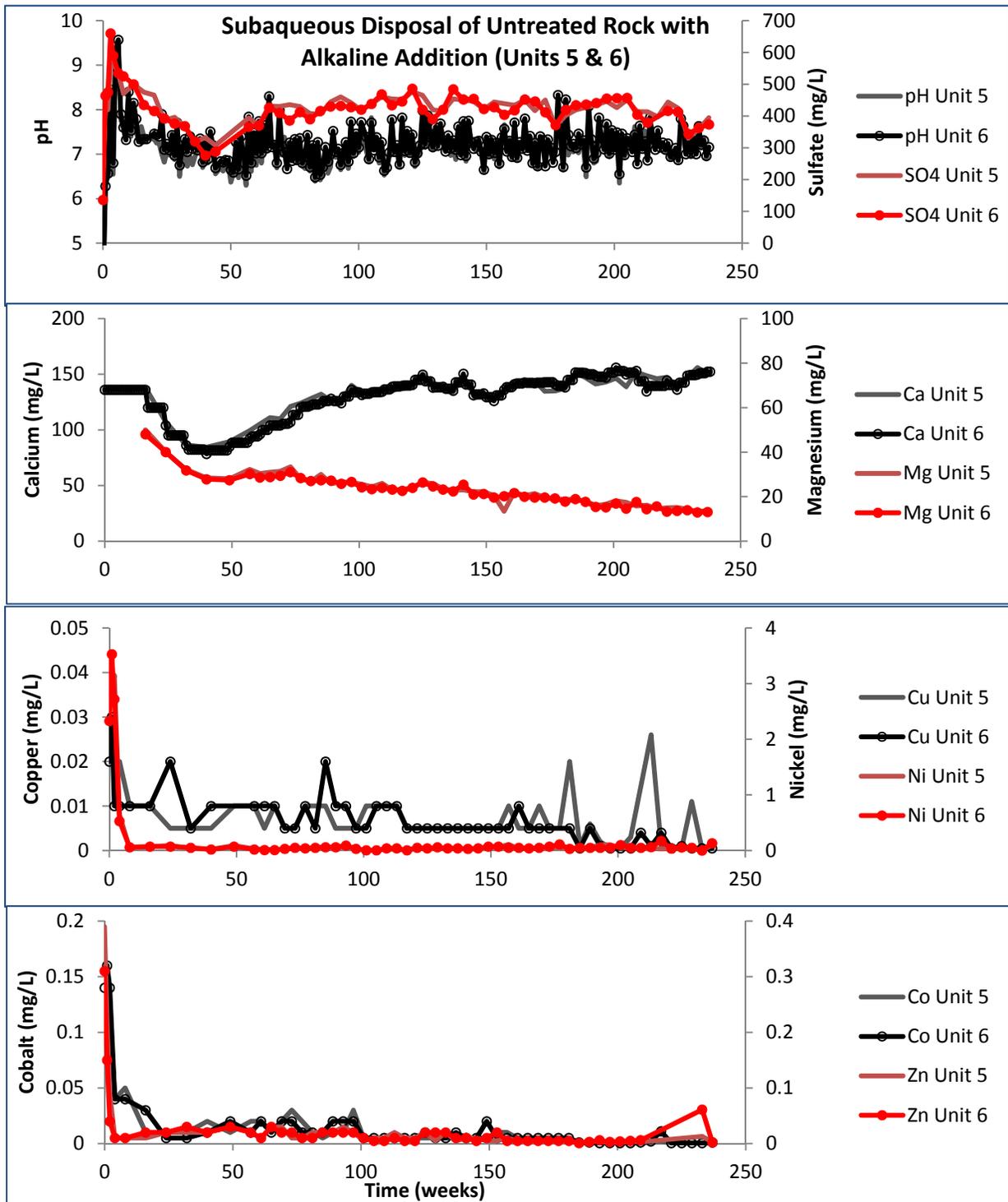


Table 11. Release rates [$\text{nmol} (\text{kg rock}\cdot\text{s})^{-1}$] for the subaqueous disposal of untreated waste rock with alkaline addition simulation (Unit 5 & 6). After the initial rinsing of oxidation products, cumulative release of sulfate was constant throughout the 238 week period of record. Negative calcium release rates indicated net removal of calcium from the water cover.

Release Rates $\text{nmol} (\text{kg rock}\cdot\text{s})^{-1}$							
Parameter	Rate Period (weeks)	Unit 5		Unit 6		N ¹	Average
		Rate	R ²	Rate	R ²		
Sulfate	0-7	11.4	0.90	12.1	0.85	6	11.7
	8-238	1.7	1.00	1.6	1.00	56	1.7
Calcium	8-238	-0.3	0.99	-0.3	0.98	51	-0.3
Magnesium	8-238	0.3	0.99	0.3	0.99	51	0.3

¹N represents the number of measured concentration values. Regression calculations used estimated values (average of previous and post measured values) to fill in weeks when samples were not taken.

Table 12. Trace metal release rates [$\text{nmol (kg rock}\cdot\text{s)}^{-1}$] for the subaqueous disposal of untreated waste rock with alkaline addition (Units 5 & 6). “Less than” values are considered an upper limit to release rates due to the high percentage of measured concentrations below detection limits.

Trace Metal	Unit	Period (weeks)	Rate	R ²	n	N ¹ (below d.l.)
Cu	5	8-238	< 0.00004	0.95	52	29
		8-91	< 0.00006	0.91	15	4
	6	91-238	< 0.00001	0.78	37	25
Ni	5	8-238	< 0.0003	0.95	52	9
	6	8-238	< 0.0003	0.95	52	10
Co	5	8-97	0.0001	0.93	17	1
		97-238	< 0.000009	0.42	35	30
	6	8-97	0.00008	0.80	17	2
		97-238	< 0.00002	0.63	35	26
Zn	5	8-97	0.0002	0.94	17	0
		97-238	< 0.00003	0.82	35	17
	6	8-97	0.0001	0.92	17	0
		97-201	< -0.0004	0.94	26	12
		201-238	< 0.00009	0.79	9	5

¹ In these experiments, trace metal concentrations were frequently below detection limits, and therefore estimated at half the detection limit. In these cases, trace metal release rates should be considered an upper bound for release and are designated with “<” in the table.

5.4. Subaqueous Disposal of Pre-treated Rock Modified by Alkaline Addition (Objective 3, Units 7 & 8)

Replication was good for the duplicate flasks of rock that was that was treated prior to subaqueous disposal, the initial pH values were elevated, reaching 9.0 at week 6, due to some residual alkalinity on the solids. The solution pH declined steadily, decreasing below 6.0 at week 9. Alkalinity was added subsequently at regular intervals to maintain circumneutral pH. Sulfate concentrations were near 20 mg/L at the beginning of the experiment, indicating, as did the elevated pH, that the pretreatment was effective in removing reaction products from rock surfaces. Subsequently, sulfate concentrations increased steadily, reaching a plateau of 450 – 550 mg/L after 75 weeks (Figure 8).

Although calculated for two different rate periods, sulfate release rates were constant at $2.0 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ (Table 13). This would be expected due to the rinsing of the rock prior to inception of the experiment. This procedure eliminated the initial “rinse –off” of soluble sulfate from the rock surface and consequent elevated sulfate release.

The addition of alkalinity in the form of a hydrated lime solution elevated calcium concentrations in the modified subaqueous test units. Calcium concentrations increased quickly from just below 50 mg/L to approximately 175 mg/L during the first 60 - 70 weeks (Figure 8). Subsequent calcium levels fluctuated between 175 - 200 mg/L. As with the untreated rock simulation, calcium was consumed, indicated by negative release rates of approximately $-0.1 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ (Table 13). Magnesium levels gradually increased throughout the experiment from initial concentrations less than 4 mg/L to approximately 17 mg/L by week 238 (Figure 8), with an average release rate of $0.2 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ (Table 13).

Trace metal concentrations were typically low, fluctuating around 0.01 – 0.02 mg/L for the duration of the experiment (Figure 8). However nickel levels increased to 0.2 – 0.3 mg/L in one of the flasks after week 187. Because of the anomalous nature of this excursion with respect to both temporal variations of nickel in this flask and nickel concentrations in the replicate, the possibility of contamination or analytical error is difficult to ignore.

Trace metal release rates were extremely low, on the order of $10^{-5} \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ with the exception of nickel ($0.0006 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, Table 14). However these rates, excluding those of nickel, were calculated from estimated concentrations in place of measured values that fell below detection limits. Therefore, these release rates should be considered an upper limit rather than absolute values. Cumulative mass release calculations indicated that less than 1% of the trace metals initially present in the rock was released into solution.

Figure 8. In the modified subaqueous disposal of pre-treated waste rock simulations (Units 7 & 8), circumneutral pH was maintained by adding alkalinity. Sulfate concentrations fluctuated around 350mg/L. Nickel concentrations increased, reaching 0.3 mg/L at 224 weeks. Roughly half of copper, cobalt and zinc concentrations were below detection limits (<0.01 mg/L).

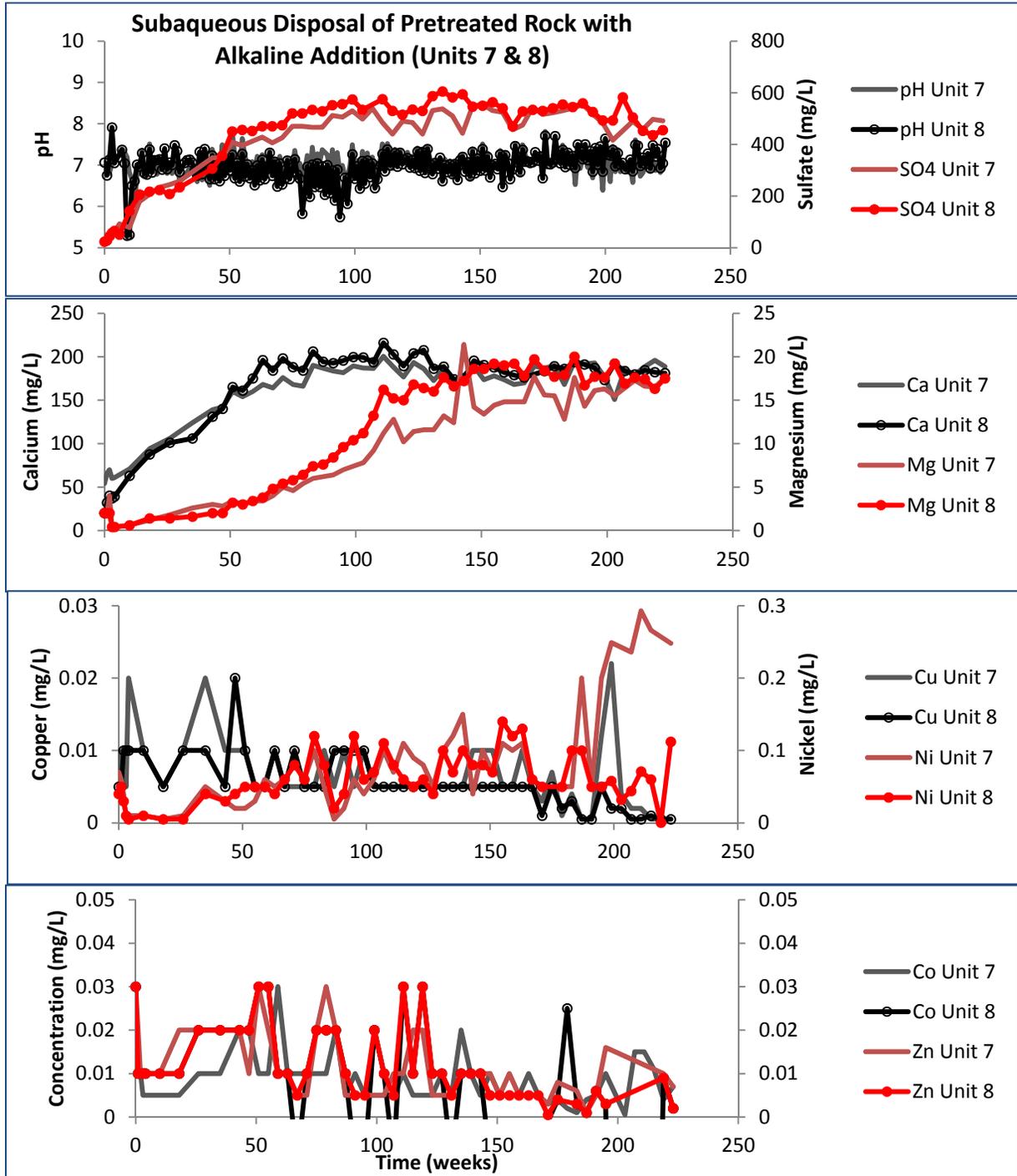


Table 13. Release rates [$\text{nmol} (\text{kg rock}\cdot\text{s})^{-1}$] for the subaqueous disposal of pretreated waste rock with alkaline addition simulation (Unit 7 & 8). After the initial rinsing of oxidation products, sulfate, calcium and magnesium release rates were relatively constant throughout the 224 week period of record.

Release Rates $\text{nmol} (\text{kg rock}\cdot\text{s})^{-1}$							
Parameter	Rate Period (weeks)	Unit 7		Unit 8		N ¹	Average
		Rate	R ²	Rate	R ²		
Sulfate	0-4	1.4	0.93	2.3	0.99	4	1.9
	5-224	2.0	1.00	2.1	1.00	52	2.0
Calcium	5-224	-0.1	0.81	-0.1	0.62	50	-0.1
Magnesium	5-224	0.2	0.99	0.3	0.99	50	0.2

¹N represents the number of measured concentration values. Regression calculations used estimated values (average of previous and post measured values) to fill in weeks when samples were not taken.

Table 14. Trace metal release rates [$\text{nmol (kg rock}\cdot\text{s)}^{-1}$] for the subaqueous disposal of pretreated waste rock with alkaline addition simulations (Units 7 & 8). “Less than” values are considered an upper limit to release rates due to the high number of concentrations below detection limits.

Trace Metal	Unit	Period (weeks)	Rate	R ²	n	N ¹ (below d.l.)
Cu	7	4-37	< 0.0001	0.75	5	1
		37-52	-0.00005	0.64	3	0
		52-224	< 0.00003	0.43	46	26
	8	4-169	< 0.00003	0.94	37	25
		169-224	< -0.00001	0.42	14	6
Ni	7	4-21	< 0.00003	0.61	3	1
		21-164	0.0005	0.97	33	1
		164-224	< 0.002	0.94	15	6
	8	4-21	< 0.00005	0.64	3	2
		21-224	0.0005	0.98	48	6
Co	7	4-133	< 0.00006	0.87	28	12
		133-224	< 0.00003	0.68	23	6
	8	4-133	< 0.00009	0.88	28	11
		133-224	< -0.00002	0.72	23	7
Zn	7	4-224	< 0.00005	0.91	51	19
	8	4-224	< 0.00005	0.87	51	17

¹ In these experiments, trace metal concentrations were frequently below detection limits, and therefore estimated at half the detection limit. In these cases, trace metal release rates should be considered an upper bound for release and are designated with “<” in the table.

5.5. Subaqueous Disposal of Leached Solids Amended with Composted Yard Waste (Objective 4, a continuation of Units 3 – 8)

At the conclusion of the initial phase of subaqueous disposal experiments (sections 4.1 – 4.4), all alkalinity addition ceased and a second phase of experiments began. The second phase involved the addition of an amendment (composted yard waste) on top of the leached waste rock in one flask of each duplicate pair from the previous experiments. The other duplicate in each case did not receive the amendment and served as a control. The objective of this phase of experiments was to determine if organic amendments to waste rock in a subaqueous environment would further inhibit sulfide mineral oxidation rates.

5.5.1. Leached Rock Controls (Units 4, 6 and 8)

Unit 4: Subaqueous Disposal

The second phase of subaqueous experiments did not involve any change in methods for Unit 4, subaqueous disposal with no further mitigation. As a result, there was little to no change in the observed water chemistry in Unit 4 (Figure 9), with pH, sulfate, and calcium levels around 3.4, 150 and 6 mg/L, respectively. Magnesium concentrations appeared to decrease somewhat from 28 mg/L initially to 13 mg/L by week 263. The apparent sudden decrease in concentrations of all species at week 268 was dilution caused by the water cover replacement (see section 3.3.3). Sulfate, calcium and magnesium release rates were steady at 0.6, 0.05 and 0.2 nmol (kg rock·s)⁻¹, respectively (Table 15). Apparent discrepancies between concentration trends and release rates resulted from removal of solutes during sampling and subsequent dilution by distilled water used to replace the volume removed during sampling (section 4.3.2).

Unit 6: Subaqueous Disposal of Untreated Rock, Previously Modified by Alkaline Addition

In Unit 6, previously modified by alkaline addition, the pH of the water cover decreased rapidly to 3.7 within 50 weeks after alkalinity additions ceased (Figure 9). The pH remained in the high 3's throughout the remaining 324 week period of record. In this first four weeks, sulfate levels decreased from 400 mg/L to 300 mg/L, where they remained fairly constant until week 150. At this time, sulfate concentrations began to gradually decrease, reaching 45 mg/L by the end of the 324 week experiment. The rate of sulfate release during the initial 140 weeks was 1.2 nmol (kg rock·s)⁻¹, and decreased to 0.6 nmol (kg rock·s)⁻¹ subsequently (Table 15).

Calcium concentrations also decreased once alkaline additions ceased (Figure 9). During the initial 50 weeks, calcium levels decreased from 140 to 60 mg/L. Subsequently, calcium continued to decrease more slowly, reaching 5 mg/L at the end of 324 weeks. The rate of calcium release also decreased from 0.5 nmol (kg rock·s)⁻¹ during the initial 140 weeks of the experiment to 0.1 nmol (kg rock·s)⁻¹ between weeks 140 and 324 (Table 15). Apparent discrepancies between concentration trends and release rates resulted from removal of solutes during sampling and subsequent dilution by distilled water used to replace the volume removed during sampling (section 4.3.2).

Magnesium concentrations initially increased concurrent with the observed pH decrease (Figure 9). Magnesium levels reached a maximum of 37 mg/L at week 135, and subsequently decreased to 4 mg/L by the end of the experiment at 324 weeks. The rate of magnesium release also decreased from 0.5 nmol (kg

$\text{rock}\cdot\text{s})^{-1}$ during the initial 140 weeks of the experiment to $0.2 \text{ nmol (kg rock}\cdot\text{s})^{-1}$ between weeks 140 and 324 (Table 15).

Copper, nickel, cobalt and zinc concentrations were observed to generally increase as the pH of the water cover decreased (Figure 9). However, limited trace metal analyses were conducted during this phase of the experiment, making it difficult to confidently identify trends.

Unit 8: Subaqueous Disposal of Pre-treated Rock Previously Modified by Alkaline Addition

Once alkalinity addition ceased to Unit 8, the pH of the water cover decreased rapidly to approximately 4 within 28 weeks (Figure 9). Sulfate concentrations decreased rapidly during the same time period, reaching a fairly constant level of 280 mg/L between weeks 28 and 140. Subsequently, sulfate levels began to decrease, reaching 43 mg/L at the end of the 324 week period of record. The rate of sulfate release during the initial 140 weeks was $1.1 \text{ nmol (kg rock}\cdot\text{s})^{-1}$, and decreased to $0.6 \text{ nmol (kg rock}\cdot\text{s})^{-1}$ subsequently (Table 15).

As expected, calcium concentrations also decreased from 165 to 80 mg/L during the initial 50 weeks after alkalinity additions ceased (Figure 9). Calcium levels continued this downward trend for the duration of the 324 weeks, reaching 5 mg/L by the end of the experiment. The rate of calcium release also decreased from $0.4 \text{ nmol (kg rock}\cdot\text{s})^{-1}$ during the initial 140 weeks of the experiment to $0.1 \text{ nmol (kg rock}\cdot\text{s})^{-1}$ between weeks 140 and 324 (Table 15). Apparent discrepancies between concentration trends and release rates resulted from removal of solutes during sampling and subsequent dilution by distilled water used to replace the volume removed during sampling (section 4.3.2).

Similar to the trend observed in Unit 6, magnesium concentrations initially increased from 16 to approximately 40 mg/L over the first 140 weeks, and subsequently decreased to 6 mg/L by 324 weeks (Figure 9). The rate of magnesium release also decreased from $0.5 \text{ nmol (kg rock}\cdot\text{s})^{-1}$ during the initial 140 weeks of the experiment to $0.3 \text{ nmol (kg rock}\cdot\text{s})^{-1}$ between weeks 140 and 324 (Table 15).

Copper, cobalt and zinc concentrations were observed to generally increase as the pH of the water cover decreased (Figure 9). Similarly, nickel concentrations increased rapidly to nearly 1 mg/L at 14 weeks, and subsequently decreased to less than 0.1 mg/L by the end of the 324 week experiment. However, limited trace metal analyses were conducted during this phase of the experiment, making it difficult to identify reliable trends.

Figure 9. After approximately 150 weeks, water quality in the subaqueous waste rock control simulations (no compost amendment, no further alkaline addition; Units 4, 6, 8; renumbered beginning at week 1) was similar to that of the previous unamended, unmodified subaqueous disposal simulation.

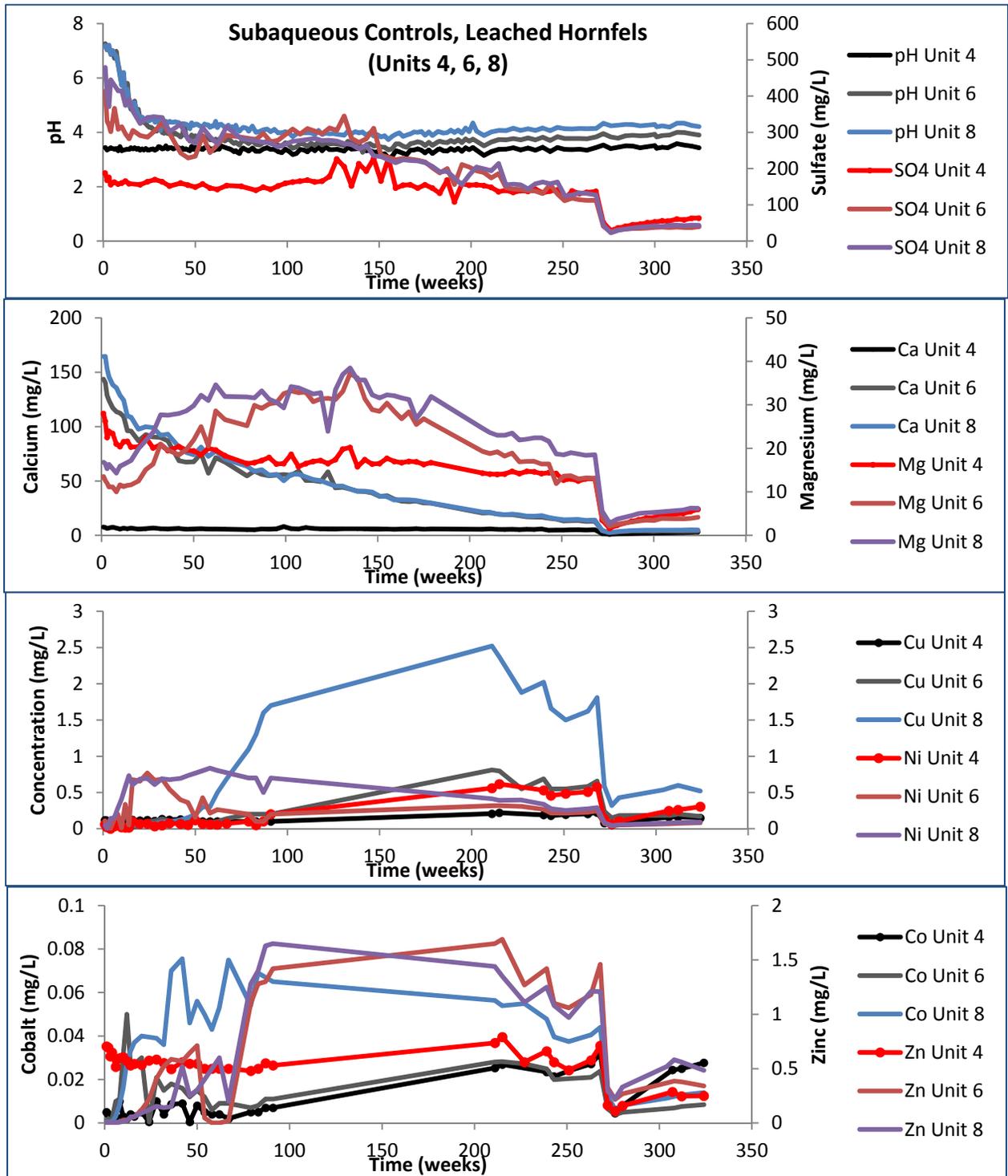


Table 15. Sulfate, calcium and magnesium release rates $\text{nmol (kg rock}\cdot\text{s)}^{-1}$: subaqueous disposal of leached waste rock controls (continuation of Units 4, 6, 8).

Simulation	Unit	Period ¹ (weeks)	Sulfate		Calcium		Magnesium	
			Rate	R ²	Rate	R ²	Rate	R ²
Leached Waste rock Control	4	1-324	0.6	1.0	0.05	1.0	0.2	0.99
	6	1-140	1.2	1.0	0.5	0.99	0.5	1.0
		140-324	0.6	0.99	0.1	0.98	0.2	0.98
	8	1-140	1.1	1.0	0.4	0.99	0.5	1.0
		140-324	0.6	0.99	0.1	0.98	0.3	0.98

¹Units were continued from the first phase of subaqueous experiments (238 weeks), but renumbered beginning at week 1 for the second phase.

5.5.2. Compost Amended Leached Rock (Units 3, 5 and 7)

Unit 3: Compost Amended Subaqueous Disposal

The initial water cover pH in Unit 3 was 4.7 (Figure 10). After the addition of a 75-g compost layer, pH immediately increased to 6.9 where it remained for 135 weeks. Subsequently, the pH began to gradually decline reaching 6.4 by the end of the experiment at 324 weeks.

Sulfate concentrations initially increased from 230 to 480 mg/L for 14 weeks after the compost addition (Figure 10), likely caused by the release of soluble or readily available sulfate present in the compost. This was followed by a period of rapid decline, with sulfate concentrations reaching a relatively constant level of 150 mg/L by week 42. The lowest of the three compost-amended sulfate release rates was observed in the previous subaqueous unit (#3) and remained constant at $0.6 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ throughout the 324 week period of record (Table 16).

Calcium and magnesium levels followed the same trend as sulfate, increasing quickly to 117 and 38 mg/L, respectively, and subsequently decreasing to steady concentrations of approximately 40 and 10 mg/L, respectively (Figure 10). Calcium and magnesium release rates were constant throughout the 324 week period of record at 0.4 and $0.2 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, respectively (Table 16).

Initially, trace metal concentrations were observed to be 0.07, 0.16, 0.008 and 0.3 mg/L for copper, nickel, cobalt and zinc, respectively (Figure 10). However, after the compost addition, these levels rapidly decreased and became fairly constant at 0.02, 0.01, 0.001 and 0.1 mg/L, respectively. Trace metal release rates were not calculated due to the large time periods when concentrations were not measured.

Unit 5: Compost Amended Subaqueous Disposal of Untreated Rock, Previously Modified by Alkaline Addition

After the addition of 75-g of compost to the leached rock, pH of the water cover remained fairly constant at 7.3 for 44 weeks (Figure 10). Subsequently, the pH began to slowly decrease reaching 6.1 by the time the water cover was replaced at week 268 (see section 3.3.3). Although sulfate concentrations initially increased above 600 mg/L in the first 6 weeks of the experiment, sulfate generally decreased, reaching 187 mg/L at week 268, when the water change occurred. The sulfate release rate during the first 200 weeks of the experiment was $1.3 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ (Table 16), which was only slightly lower than that observed in the previous phase prior to compost addition. However, between weeks 200 and 324, the sulfate release rate decreased to $0.8 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$.

Both calcium and magnesium concentrations gradually declined over the 324 week period of record, reaching 26 and 8 mg/L, respectively (Figure 10). Initial calcium and magnesium release rates of 0.7 and $0.4 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, respectively, decreased by roughly 50% after week 200 (Table 16). Apparent discrepancies between concentration trends and release rates resulted from removal of solutes during sampling and subsequent dilution by distilled water used to replace the volume removed during sampling (section 4.3.2).

Copper, nickel and cobalt concentrations remained fairly constant at approximately 0.005, 0.01, 0.001 mg/L, respectively (Figure 10). Zinc levels appeared to increase slightly from 0.01 to 0.1 mg/L by the end

of the 324 week period of record. Trace metal release rates were not calculated due to the large time periods when concentrations were not measured.

Unit 7: Compost Amended Subaqueous Disposal of Pre-treated Rock, Previously Modified by Alkaline Addition

Despite the addition of the 75-g layer of compost, the water cover pH in Unit 7 rapidly decreased to approximately 4.5 at week 19 (Figure 10). Thus an additional 75-g dose of compost was added to Unit 7 at week 58. Within two weeks of the second compost addition, the pH had rebounded to 7.6, where it remained for the 324 week period of record.

Concurrent with the pH depression, sulfate concentrations in Unit 7 increased quickly to 900 mg/L (Figure 10). Subsequent to the second dose of compost, sulfate concentrations began to decrease, quickly reaching 150 mg/L by week 160, and then more slowly reaching approximately 50 mg/L by the end of the experiment at week 324. The sulfate release rate during the initial 70 weeks was elevated at $3.3 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ (Table 16). Subsequent to the second compost dose, the sulfate release rate decreased to $0.5 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$.

Calcium and magnesium levels followed a similar trend to that of sulfate, increasing to 340 and 70 mg/L, respectively, and subsequently decreasing to steady concentrations of approximately 40 and 11 mg/L, respectively (Figure 10). Calcium and magnesium release rates during the initial 70 weeks were elevated at 2.4 and $1.2 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, respectively (Table 16). However, these levels decreased to 0.3 and $0.2 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, respectively, for the remainder of the 324 week experiment.

Copper and nickel concentrations decreased from 0.02 and 0.06 mg/L respectively to less than 0.005 mg/L each by the end of 324 weeks (Figure 10). Cobalt concentrations remained fairly constant near detection limits at 0.001 mg/L. Zinc levels appeared to increase slightly from 0.01 to 0.1 mg/L by the end of the 324 week period of record. Trace metal release rates were not calculated due to the large time periods when concentrations were not measured.

Figure 10. While pH remained near neutral and trace metal concentrations were low, compost addition had little effect on sulfate, calcium and magnesium levels when compared to the controls. (Units 3, 5, 7; renumbered beginning at week 1)

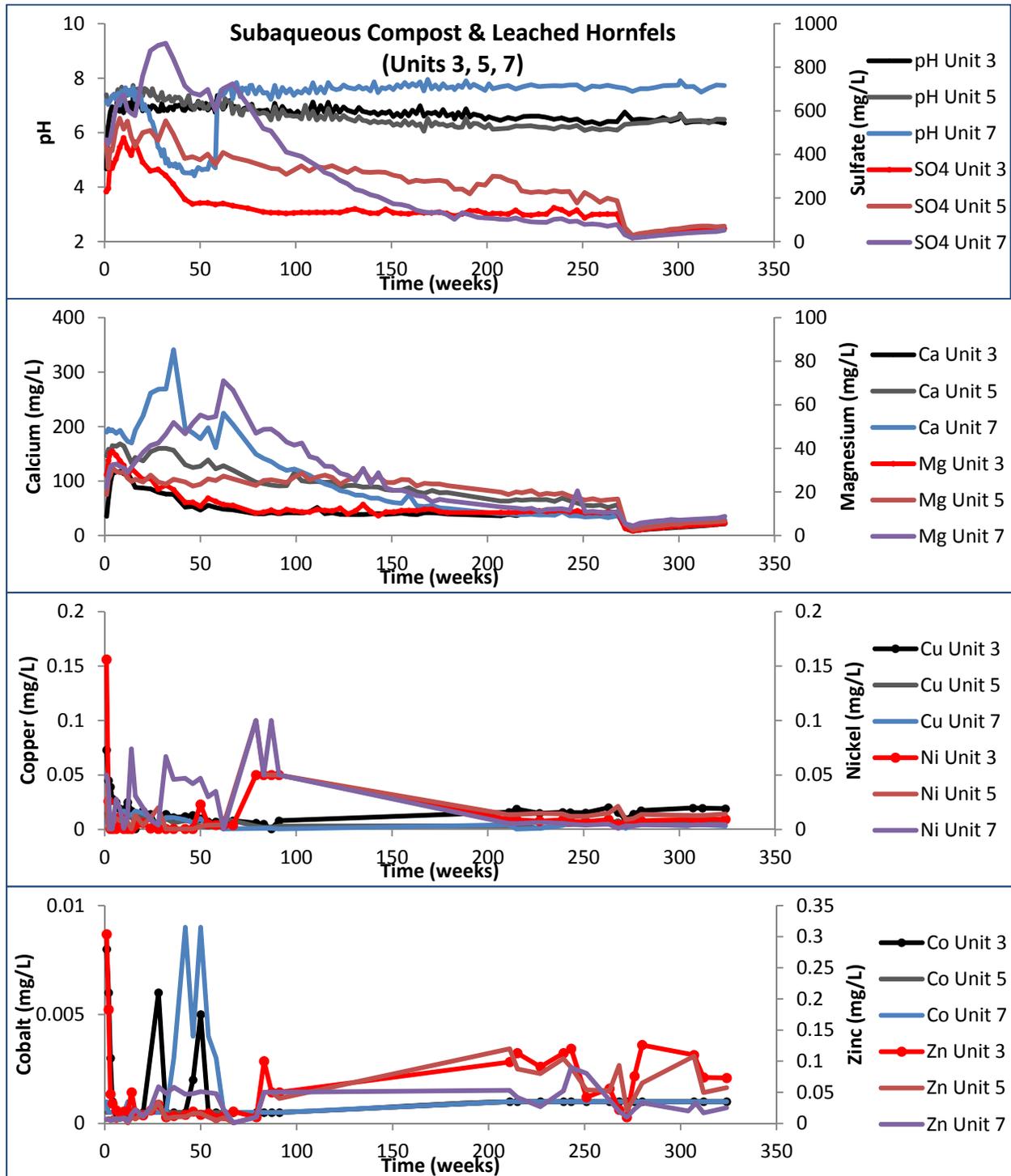


Table 16. Sulfate, calcium and magnesium release rates $\text{nmol (kg rock}\cdot\text{s)}^{-1}$: subaqueous disposal of leached waste rock amended with composted yard waste (continuation of Units 3 - 8).

Simulation	Unit	Period ¹ (weeks)	Sulfate		Calcium		Magnesium	
			Rate	R ²	Rate	R ²	Rate	R ²
Compost & Leached Waste rock	3	10–324	0.6	0.99	0.4	1.0	0.2	1.0
	5	30-200	1.3	0.99	0.7	0.99	0.4	1.00
		200–324	0.8	0.98	0.4	0.98	0.2	0.99
	7 ²	0 – 70	3.3	0.99	2.4	0.97	1.2	0.99
		70-324	0.5	0.93	0.3	0.98	0.2	0.97

¹Units were continued from the first phase of subaqueous experiments, but renumbered beginning at week 1.

²an additional 75 g of compost was added at week 58 to maintain neutral pH.

5.6. Subaqueous Disposal of Fresh Solids Amended with Compost (Objective 4, Units 9 – 14)

A third phase of experiments was designed to measure the effect of compost on sulfate release rates from fresh Virginia hornfels waste rock in a subaqueous environment. This was accomplished using six four-liter beakers: two compost controls, two hornfels controls and two compost and hornfels test beakers.

5.6.1. Compost Controls (Units 9, 10)

Controls containing compost only (units 9 and 10) were conducted for 20 weeks in order to determine the solute release from the compost. Water quality results for both controls were in good agreement. The pH was measured weekly and remained in the 7's (Figure 11). Sulfate levels ranged from 10 – 35 mg/L with release rates between 0.2 and 0.8 nmol (kg rock·s)⁻¹ (Table 17). This accounted for approximately 142 mg (1.5 mmol) of sulfate released into solution, or 21% of the total sulfur present in the compost (5.03 mmol total S).

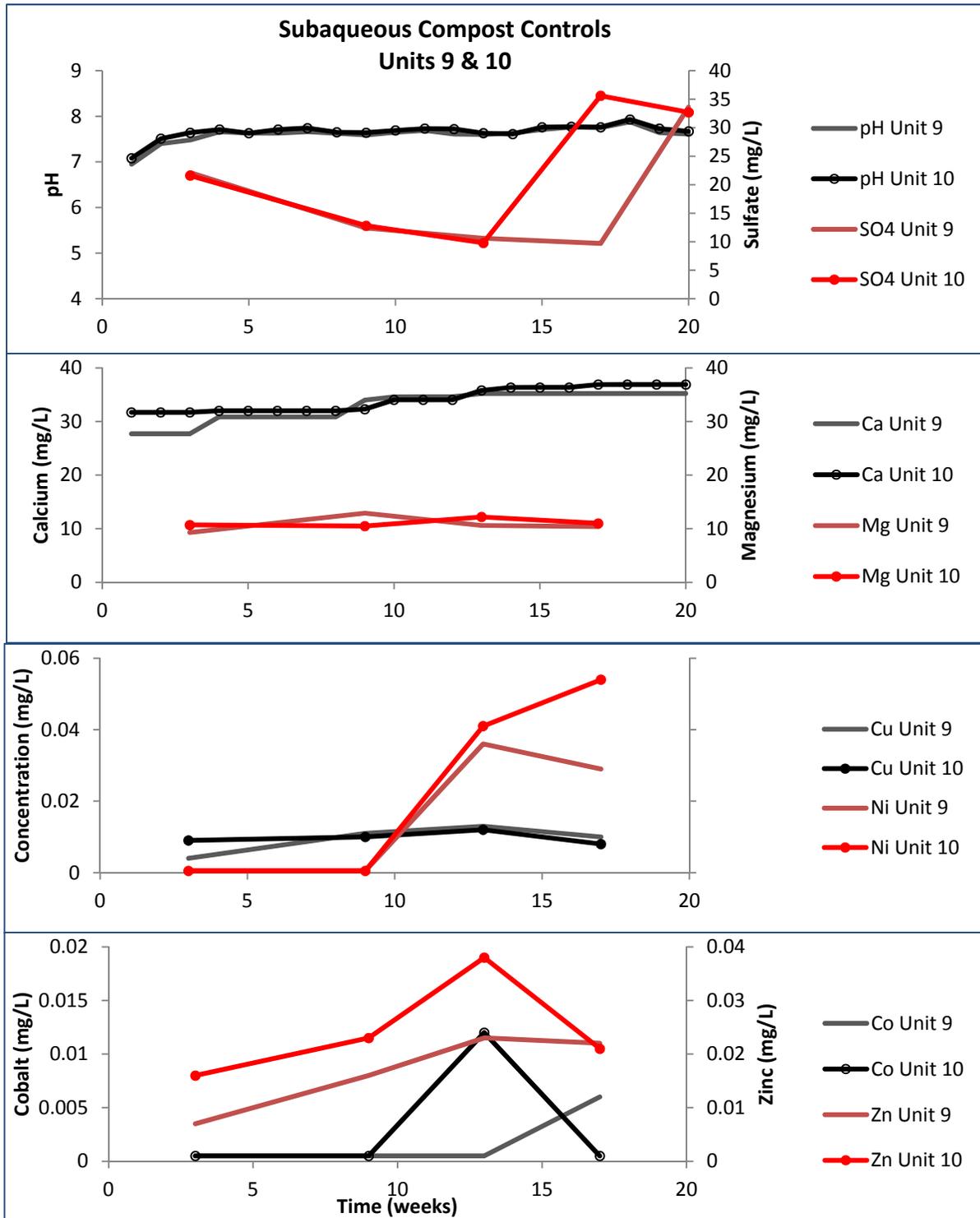
Calcium and magnesium levels averaged 34 and 11 mg/L, respectively (Figure 11). Copper, nickel, cobalt and zinc levels of roughly 0.01, 0.02, 0.003, and 0.02 mg/L (n = 8, 4 for each replicate). However, four of the nickel values and six of the cobalt values were below detection limits of 0.001 mg/L and were estimated as half the detection limit.

Table 17. Sulfate, calcium and magnesium release rates nmol (kg compost·s)⁻¹ for the compost controls (Units 9 and 10. 75-g compost).

Release Rates nmol (kg compost·s) ⁻¹							
Species	Period (weeks)	Replicate 1	R ²	Replicate 2	R ²	Average	N ¹
Sulfate	1-20	0.2	0.22	0.8	0.67	0.5	6
Calcium	1-20	2.2	0.96	2.0	0.95	2.1	6
Magnesium	1-20	0.8	0.80	0.9	0.94	0.8	6

¹N used to calculated release rates.

Figure 11. Water quality of the Subaqueous Compost Controls: 75-g composted yard waste in 3.6 L water.



5.6.2. Fresh Waste Rock Controls (Units 11, 12)

Similar to the previous results from the subaqueous disposal simulation (Units 3 and 4), the pH of the water layer above the fresh waste rock controls quickly decreased to around 3.3 (Figure 12). Sulfate concentration increased to approximately 300 mg/L in 80 weeks, and subsequently decreased gradually to 170 mg/L at week 209. At this time, the water was removed from the flasks and replaced with distilled water (see section 3.3.4). Replacing the water resulted in sulfate concentrations decreasing to 50 - 60 mg/L. Sulfate release rates for the two replicates were in good agreement at $1.7 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ over the first 95 weeks of the experiment (Table 18). Sulfate release rates decreased sharply to $0.6 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ after 95 weeks. This was likely due to the formation of precipitates or coatings at the mineral surface and subsequent inhibition of oxygen and sulfide oxidation.

Calcium and magnesium concentrations followed a similar pattern to that of sulfate, increasing quickly 25 – 30 mg/L and then steadily decreasing to 10 and 20 mg/L, respectively (Figure 12). Calcium and magnesium release rates averaged 0.3 and 0.6 $\text{nmol (kg rock}\cdot\text{s)}^{-1}$, respectively, during the first 95 weeks, decreasing to 0.04 and 0.2 $\text{nmol (kg rock}\cdot\text{s)}^{-1}$ respectively, for the remainder of the experiment (Table 18).

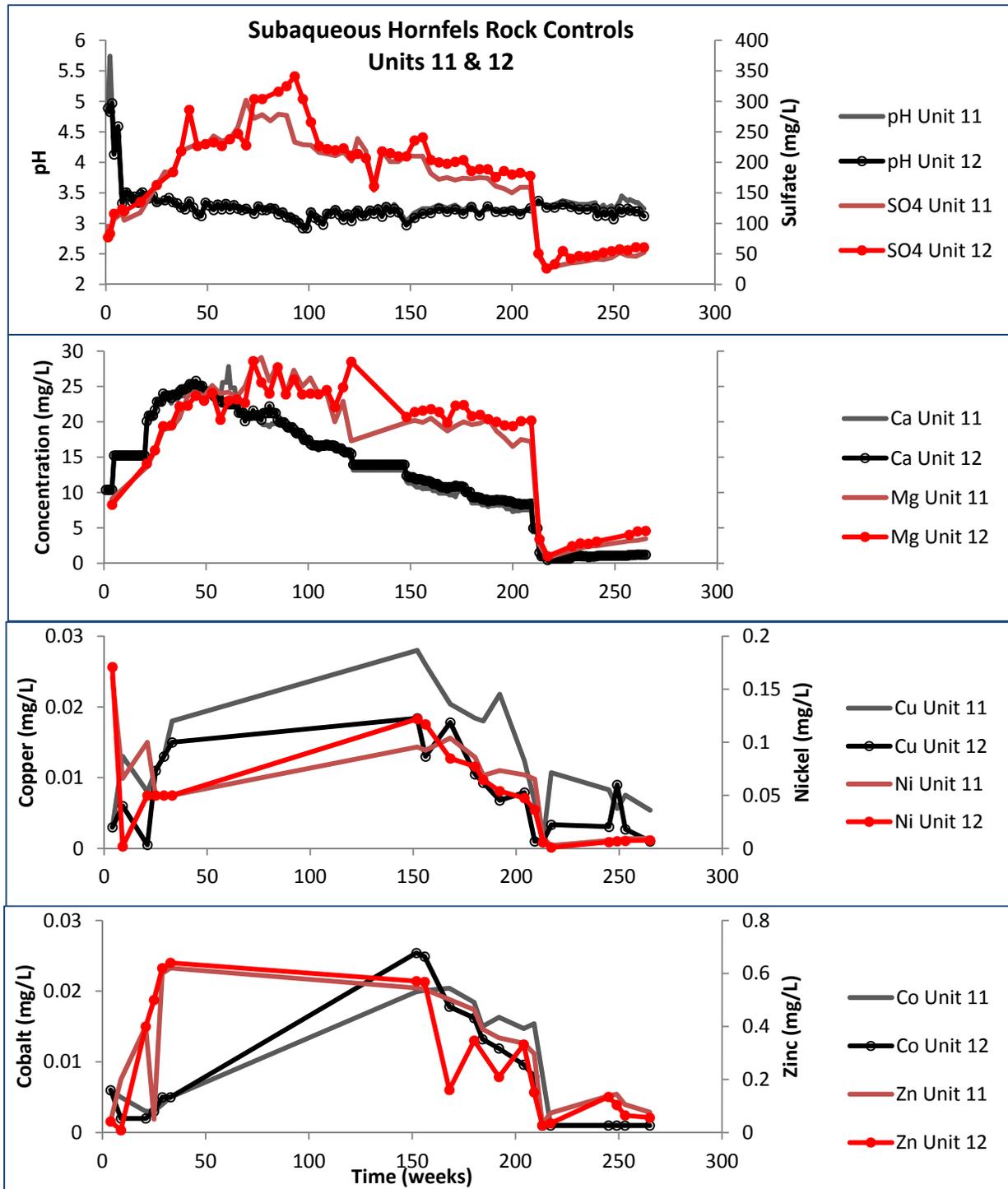
Trace metal levels were not measured between weeks 34 and 148. However, all four trace metal concentrations, particularly nickel and zinc, appeared to be decreasing after sampling resumed at week 148. Nickel and zinc reached maximum measured concentrations of 0.1 and 0.5 mg/L, respectively at week 148 (Figure 12).

Table 18. Sulfate, calcium and magnesium release rates $\text{nmol (kg rock}\cdot\text{s)}^{-1}$ for the subaqueous disposal of fresh waste rock controls (Units 11 and 12).

Species	Period (weeks)	Release Rates $\text{nmol (kg rock}\cdot\text{s)}^{-1}$					
		Replicate 1	R ²	Replicate 2	R ²	Average	N ¹
Sulfate	1-95	1.6	0.99	1.7	0.99	1.7	23
	95-265	0.5	0.98	0.6	0.99	0.6	43
Calcium	1-95	0.3	0.93	0.3	0.93	0.3	20
	95-265	0.04	0.92	0.04	0.93	0.04	32
Magnesium	1-95	0.6	0.99	0.6	0.98	0.6	20
	95-265	0.2	0.96	0.2	0.97	0.2	32

¹N used to calculate release rates.

Figure 12. After approximately 80 weeks, pH and sulfate levels in the fresh hornfels waste rock controls (Units 11 & 12) were similar to that observed in previous the subaqueous simulations (compare to figure 4.2.1).



5.6.3. Fresh Waste rock Amended with Composted Yard Waste (Units 13, 14)

Although the pH of the water above the fresh waste rock amended with composted yard waste was above 7.0 at the beginning of the experiment, it began to decrease at roughly 35 weeks and fell below the water quality standard of 6.0 after 105 weeks (Figure 13). This steady decline in pH continued for 265 weeks, reaching 4.0 – 4.3 by the end of the experiment.

Sulfate concentrations in these simulations gradually increased to approximately 300 mg/L over the first 209 weeks (Figure 13). After the removal and replacement of water at 209 weeks, these levels dropped to 30 mg/L. Subsequently, sulfate levels began to increase again, reaching roughly 150 mg/L by the end of the experiment at week 265.

Overall sulfate release rates for the combined fresh waste rock and compost simulations were 1.4 and 1.6 nmol (kg rock·s)⁻¹ over the 265 week period of record (Table 19). Sulfate release rates were fairly steady over the period of record with the exception of an unexplained rate increase between weeks 85 and 130 (Table 19). It was supposed that this anomaly was due to unusually high sample volumes recorded in the original data file during this time period. However, lab notes did not provide any insight. Alternatively, there may have been a component of the compost amendment that temporarily enhanced oxidation, although no direct evidence to support this speculation has been identified. This anomalous period involved 5 – 12 actual measured sulfate values and it did not have a large influence on sulfate release rates or the conclusions drawn from these results. Consequently, these values are presented in Table 19, but ignored in subsequent discussion.

Calcium and magnesium levels in the fresh solids amended with compost simulations gradually increased to approximately 85 and 20 mg/L, respectively, during the first 209 weeks (Figure 13). After the removal and replacement of water at 209 weeks, these levels dropped to 10 and 2 mg/L, respectively, and subsequently increasing until the end of the experiment at 265 weeks. Calcium and magnesium release rates displayed the same anomalous pattern as described for sulfate. However over the period of record, calcium and magnesium release rates were reasonably constant at 1.0 and 0.4 nmol (kg rock·s)⁻¹, respectively (Table 19).

Trace metal concentrations were generally low, increasing in the order Co < Cu < Ni < Zn (Figure 13). Cobalt concentrations were near or below detection (0.001 mg/L) throughout the experiment. Copper concentrations were typically below 0.005 mg/L, and the ceiling for nickel concentrations was about an order of magnitude higher. Zinc concentrations tended to increase throughout the experiment, reaching 0.3 mg/L as pH decreased to the low 4's (Figure 13).

Figure 13. Subaqueous disposal of fresh waste rock with composted yard waste (Units 13 & 14) resulted in low (4 – 4.5) pH and increasing sulfate, calcium and magnesium concentrations.

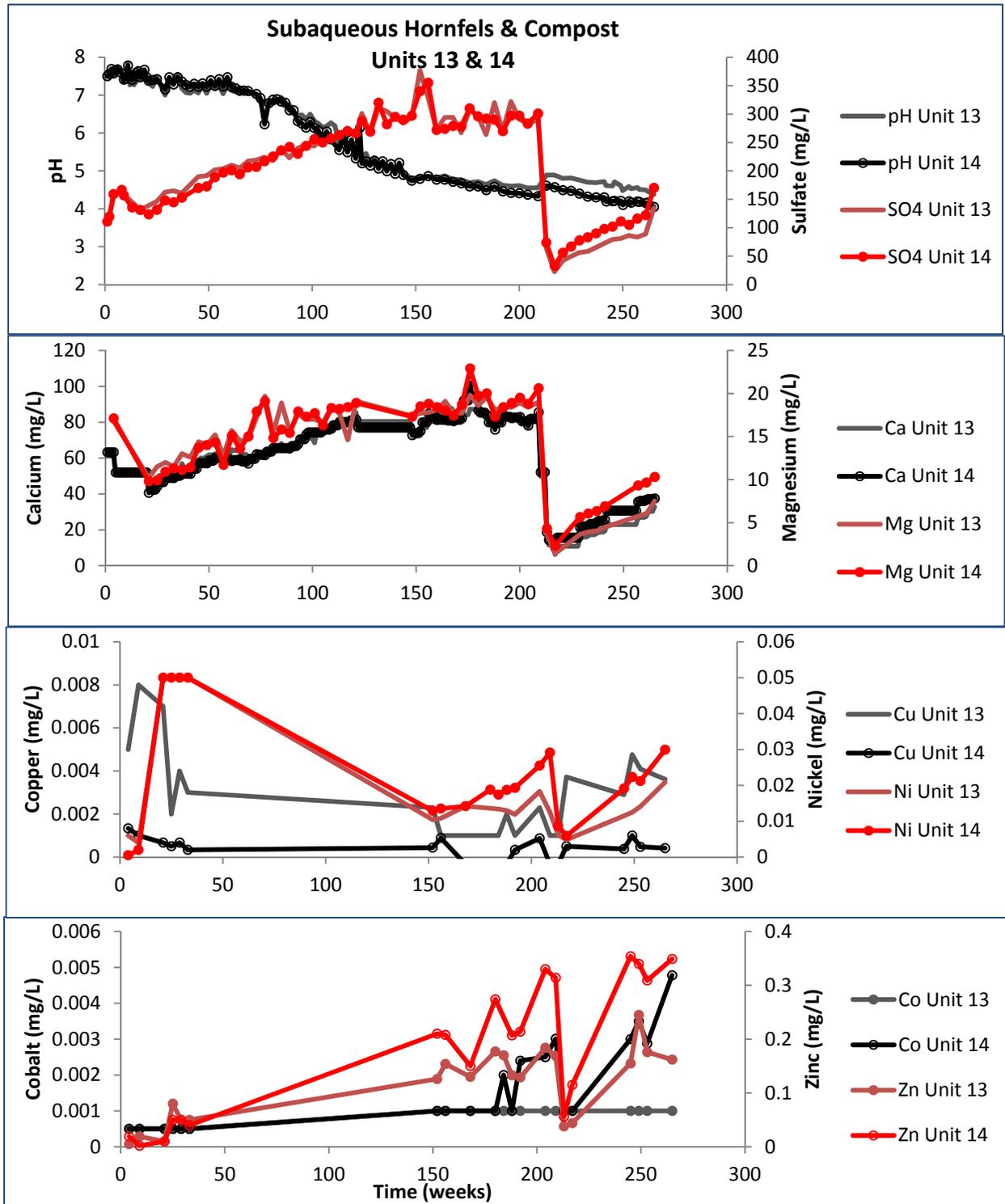


Table 19. Sulfate release rates averaged $1.5 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, overall, for the subaqueous disposal of fresh waste rock amended with composted yard waste (Units 13 and 14).

Release Rates $\text{nmol (kg rock}\cdot\text{s)}^{-1}$									
Parameter	Unit 13				Unit 14				Average
	Rate Period (weeks)	Rate	R ²	N ¹	Rate Period (weeks)	Rate	R ²	N ¹	
Sulfate	1-265	1.6	0.99	67	1-265	1.4	0.99	61	1.5
	1-85	1.4	0.99	19	1-85	1.3	0.99	20	
	85-133	2.8	1.0	12	85-105	3.2	0.99	5	
	133-265	1.0	0.97	36	105-265	1.1	0.99	36	
Calcium	1-265	1.1	0.99	52	1-265	1.0	0.99	52	1.0
	1-85	0.9	0.98	18	1-85	0.9	0.99	18	
	85-133	2.0	0.99	10	85-105	2.5	1.0	6	
	133-265	0.7	0.98	25	105-265	0.8	0.99	30	
Magnesium	1-265	0.4	0.99	52	1-265	0.4	0.99	52	0.4
	1-85	0.4	0.99	18	1-85	0.4	0.99	18	
	85-133	0.7	0.99	10	85-105	0.9	0.99	6	
	133-265	0.3	0.98	25	105-265	0.3	0.99	30	

¹N used to calculate release rates.

6. Discussion

6.1. Conceptual Framework for Pyrrhotite Oxidation

The rate of pyrrhotite oxidation can be reduced if pyrrhotite-bearing rock is stored under water, likely in a mined-out pit. The main factor behind the success of subaqueous disposal of mine waste over that of surface disposal is the slow diffusion rate of oxygen in water, almost 10,000 times slower than in air. Critical considerations regarding subaqueous disposal are described by the following conceptual framework. Pyrrhotite oxidation occurs through a series of steps by which iron is gradually removed from the crystal structure. Conceptually, the pyrrhotite structure passes through numerous intermediate forms from Fe_7S_8 to FeS_2 to Fe_yS , where $y < 0.5$ (Nicholson and Scharer, 1994; Janzen 1996; Pratt et al., 1994a and b). In addition to the release of Fe^{II} , acid and trace metals are released into solution as pyrrhotite oxidizes. As acid is generated, the pH of drainage or a water cover will decrease. Once the pH decreases below 4, biological mediation becomes predominant and accelerates the rate of sulfide mineral oxidation (Singer and Stumm 1970, Kleinmann et al. 1981, Nordstrom 1982).

At any point during oxidation, Fe^{II} can be further oxidized to Fe^{III} , which precipitates as an iron oxyhydroxide (e.g. FeOOH). As oxidation proceeds at the crystal surface, an iron oxyhydroxide layer forms. Iron-depleted, or alternately, sulfur-enriched intermediates form in layers between the oxide coating and unreacted pyrrhotite. Furthermore, iron oxyhydroxides may precipitate from solution, forming a rust-colored coating at the mineral-water interface. Subsequent reaction requires iron to diffuse through these surficial and/or interfacial iron oxyhydroxide layers, decreasing the rate at which reaction occurs.

Sulfate release rates from thin layers of fresh and leached waste rock have been calculated for the following simulated disposal objectives:

1. Subaerial (on-land) disposal (fresh rock only),
2. Subaqueous disposal with no further mitigative measures,
3. Subaqueous disposal modified by alkaline addition to maintain circumneutral pH, and
4. Subaqueous disposal amended with an organic layer of composted yard waste.

Thin layers of rock were used to allow more precise determination of reaction rates over time.

Because the sulfate release was largely due to pyrrhotite oxidation and the pyrrhotite surface area present varied among samples, this variation was considered to strictly compare sulfate release rates. Differences in pyrrhotite surface area resulted from differences in sample mass and pyrrhotite content of samples. Rates were normalized using two methods. Strictly for the purposes of calculations used within this presentation, sulfate release rates were normalized for rock mass. This method used the fewest assumptions, and therefore, was considered to provide the most straight forward comparison of pyrrhotite oxidation rates.

The second method normalized sulfate release rates to pyrrhotite mineral surface area. Pyrrhotite oxidation rates were expressed as a function of mathematically derived pyrrhotite surface area (0.0162 m^2/g rock, 0.0188 m^2/g rock and 0.0178 m^2/g rock for units 1-6, 7-8 and 11-14, respectively). Pyrrhotite surface areas were calculated geometrically using a mean diameter (d) = 1×10^{-4} m, specific gravity = 4.6, surface roughness factor = 1, and assumed all reported sulfur to be present as pyrrhotite. Pyrrhotite oxidation rates using these values can be compared more readily with rates found in the literature. Data from Janzen et al.

(2000) suggest an approximate range of 10 to 28 for the surface roughness coefficient of pyrrhotite grains of 100 μm in diameter. The geometric mean of these values is about 17. Using this roughness coefficient yields a pyrrhotite oxidation rate 0.060 times that calculated using a roughness coefficient of 1.

6.2. Objective 1: Subaerial Simulation

The results from the initial 238 weeks of the subaerial simulation are presented in section 4.1. However, dissolution in the subaerial simulations continued for 562 weeks. No modifications were made to the subaerial simulations during this time period. As stated in section 4.1, after approximately 100 weeks of dissolution, sulfate release rates increased sharply to $9.5 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, concurrent with a decrease in pH below 3.0 (Table 7). This was assumed to be due to biologically-mediated sulfide mineral oxidation and continued until approximately week 300, at which point, sulfate release rates decreased to approximately $0.4 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$. Normalized sulfate release rates for the pyrrhotite surface area appear in Table 20. These are in good agreement with those previously determined by Lapakko (1994) and based on the first 120 weeks of this experiment.

There are three factors that may have contributed to the observed decrease in sulfate release rates after 300 weeks in the subaerial environment. First, it may be that the apparent reduction in sulfate release was caused by the formation of a secondary mineral such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). When sulfate and calcium are present in large quantities in solution, saturation and precipitation of gypsum is possible. However, comparison of calcium and sulfate concentrations to the gypsum solubility product ($\log Q/K$) indicated that the subaerial simulations had not reached saturation with respect to gypsum (Appendix B3).

Second, cumulative sulfate release calculations indicated that roughly 65 to 88% of the available sulfur was released from the waste rock over the first 300 weeks of the experiment (Figure 14). This wide range should be considered an estimate due to the fact that laboratory notes on the experiment noted problems with filtration and spilling of solids (Appendix E1). However, given the calculated range of depletion, it can be reasonable estimated that roughly 75% of the sulfide minerals had oxidized at the time of the sulfate release rate decrease. Thus, reaction would be expected to slow because the pyrrhotite surface area had decreased over the 6 $\frac{1}{2}$ year period of record.

Third, visual evidence in the form of rust-colored particles suggested the presence of precipitates. This precipitate may occur either as a coating on the mineral surface (or as sediment in the bottom of the subaqueous reaction vessels) with a consequent inhibition of oxygen transport to the mineral surface. During the initial mineral analysis of these solids, alteration shells presumed to be iron oxyhydroxides were identified on pyrrhotite mineral grains using SEM (Figure 1), and such coatings likely developed further as oxidation proceeded. Similar iron oxyhydroxide coatings have been observed in SEM analysis of leached Duluth Complex solids from comparable MN DNR laboratory studies (Figure 15). In addition to MN DNR studies, iron oxyhydroxide alteration shells on oxidized waste rock and tailings have been reported in the literature (Shaw et al. 1998; Jambor 2003; Belzile et al. 2004). While it is likely that iron oxyhydroxide coatings and/or precipitates have formed on the waste rock used in this experiment, it had not been confirmed at the time of this report. Given that sulfate release suggested substantial sulfur depletion in the rock, both sulfur depletion and iron oxyhydroxide coating explanations for the observed decrease in pyrrhotite oxidation rates are reasonable and cannot be discounted.

Table 20. Average normalized pyrrhotite oxidation rates for the subaerial simulations. Pyrrhotite oxidation rates increased nearly five times after 100 weeks of dissolution, presumably biologically mediated. Lapakko (1994) reported an oxidation rate of 5.6 – 13 nmol (kg rock·s)⁻¹ for weeks 100 – 120, which is in good agreement with the current average of 9.5 nmol (kg rock·s)⁻¹ for weeks 100 – 300. (Values used for pyrrhotite surface area calculation: d = 0.0001 m, specific gravity = 4.6, specific surface area = 0.0016 m²/g, surface roughness factor = 1)

Description	Approximate Time Period (weeks)	Average Subaerial Pyrrhotite Oxidation Rates	
		Normalized to rock mass [nmol (kg rock·s) ⁻¹]	Normalized to surface area [nmol (m ² pyrr·s) ⁻¹]
“Rinse off”	0-10	4.3	2.6
Apparent abiotic oxidation	10-100	2.0	1.3
Biologically-mediated oxidation	100-300	9.5	5.9
Sulfur depletion and/or coating	300-560	0.4	0.2

Figure 14. Approximately 75% of the sulfide minerals in the waste rock were depleted within 300 weeks based on cumulative sulfate release from the subaerial simulation experiments. (See section 4.3 and Appendix E1 for a description of relevant laboratory errors and explanation of estimation.)

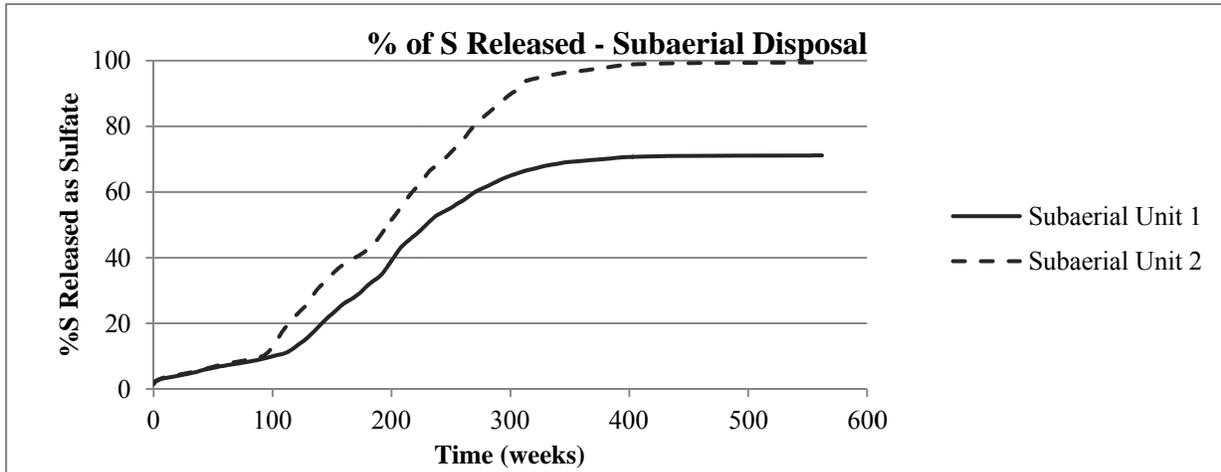
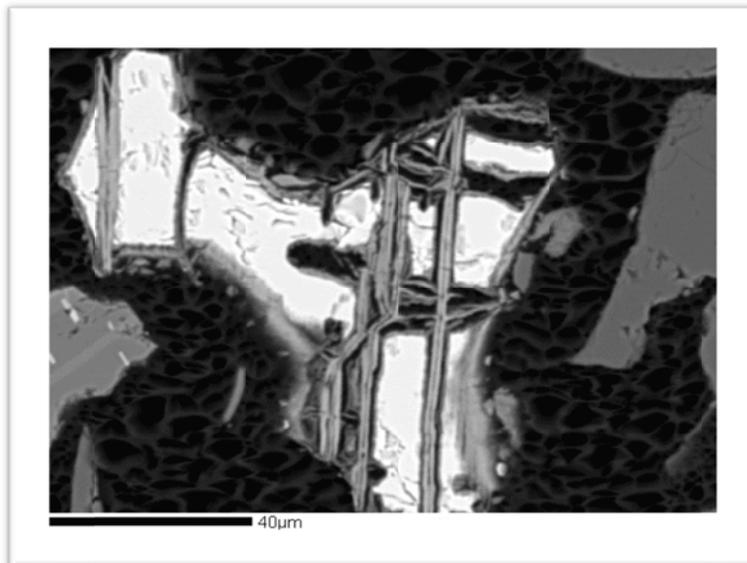


Figure 15. Iron oxyhydroxide coatings (light gray) surrounding a pyrrhotite grain (bright white) present in 0.58 %S Duluth Complex rock, approximately 50 – 150 μm , leached for 328 weeks (MN DNR unpublished data).



6.3. Objectives 2 and 3: Comparison of Release Rates for Subaqueous Disposal Simulations

The initial phase of experiments examined three different subaqueous objectives:

1. subaqueous disposal with no further mitigative measures,
2. subaqueous disposal of waste rock modified with alkaline addition to the water cover to maintain circumneutral pH, and
3. subaqueous disposal of waste rock pretreated to remove residual oxidation products and modified with alkaline addition to the water cover to maintain circumneutral pH.

During the 24 week “rinse-off” period, elevated concentrations of sulfate and other solutes were observed in the subaqueous disposal with no further mitigation and subaqueous disposal of untreated rock with alkaline addition simulations. This release was attributed to the removal of soluble oxidation products that accumulated on the rock prior to the experiment. The amount of sulfate released to solution from the rock surfaces ranged from 5 to 8 mg per gram rock. As expected, this initial period of elevated solute release was not observed in the subaqueous disposal of pretreated waste rock.

Subsequent to the initial “rinse-off” period, the aqueous sulfate observed was attributed to sulfide mineral oxidation under specified reaction conditions. The data indicated that pyrrhotite can oxidize in a subaqueous environment with a consequent generation of acid and provided rates for that oxidation. Average sulfate release rates from the three different subaqueous disposal of waste rock reaction environments ranged from 1.3 to 2.0 nmol (kg rock·s)⁻¹ (Table 21). These values are in good agreement with those determined in previous work (Lapakko 1994), and approximated apparent abiotic oxidation rates observed in the subaerial simulations. This indicated that the depth of rock in the present experiment was not deep enough for oxygen diffusion to limit the abiotic rate of pyrrhotite oxidation. Thus, rates observed were representative of those occurring at the water-rock interface.

It appears that in each of the subaqueous disposal simulations, pyrrhotite oxidation rates remained in a range expected for abiotic oxidation and never entered a period of biological mediation (Figure 16). By comparison, a sharp increase in sulfate release rates as the drainage pH of the subaerial simulations decreased below roughly 3.7 indicated biologically-mediated sulfide mineral oxidation. This was not observed in any of the subaqueous simulations, thus it was concluded that water covers inhibited biologically-mediated sulfide mineral oxidation.

Subsequent to the period of oxidation ending at approximately 200 weeks, sulfate release rates in a simple subaqueous environment (Units 3 & 4) were observed to decrease to 0.3 nmol (kg rock·s)⁻¹ (Table 9). A similar decrease to 0.6 nmol (kg rock·s)⁻¹ was observed in subaqueous units 6 and 8, which received alkalinity during the first phase (238 and 224 weeks, respectively) of the experiment (Table 15). However the decrease did not occur until 140 weeks after alkaline additions had been terminated. As discussed in section 5.1 (Subaerial Simulations) there are two likely causes for the observed decrease in oxidation rates: sulfide mineral depletion and the formation of iron oxyhydroxide coatings and/or precipitates. Cumulative sulfate release calculations indicated that less than 15% of the available sulfur in the waste rock had been released (Figure 17). Therefore, it is unlikely that mineral depletion was the only cause of decreased sulfate release rates, unlike the subaerial simulations where mineral depletion was likely the major factor for the observed decrease. Furthermore, visual inspection of the reaction units indicated the formation of

precipitates on the rock surfaces (Figure 18). Precipitates and/or coatings (e.g. iron oxyhydroxides) forming on the mineral surface could effectively inhibit oxygen diffusion to fresh sulfide mineral surfaces, and consequently, diminish pyrrhotite oxidation and acid production.

In summary, these laboratory batch simulations demonstrated that subaqueous disposal reduced the rate of sulfide mineral oxidation when compared to subaerial disposal. Because the rock layers in the subaqueous environment were thin, sulfate release could be attributed to the known mass of rock at the water-rock interface. Rock disposed under water did not exhibit the increase in oxidation rate (attributed to microbial mediation) observed for the rock disposed subaerially. Subaqueous disposal appears to have the additional advantage of more readily reducing oxidation by the formation of iron oxyhydroxide coatings, leaving a greater fraction of the unoxidized sulfide mineral to react at the slower rate. The addition of alkalinity to the overlying water provided no further benefit. However it does provide a means of estimating the alkaline inputs required to maintain circumneutral pH in a full-scale subaqueous disposal setting.

Table 21. Normalized rates of sulfate release used to determine apparent abiotic pyrrhotite oxidation rates only. Rate periods for biologically-mediated oxidation and iron oxyhydroxide coating/precipitate inhibition are not included in this table. Visually determined periods of linear cumulative sulfate release were used to calculate oxidation rates.

Objective	Units	Average Pyrrhotite Oxidation Rates ¹ “apparent abiotic oxidation”	
		Normalized to rock mass [nmol (kg rock·s) ⁻¹]	Normalized to surface area ² [nmol (m ² pyrr·s) ⁻¹]
1. Subaerial Disposal	1, 2	2.0	1.3
2. Subaqueous Disposal (no further mitigative measures)	3, 4	1.3	0.8
3. Modified Subaqueous Disposal (alkaline addition to maintain pH, untreated rock)	5, 6	1.7	1.0
3. Modified Subaqueous Disposal (alkaline addition, pretreated rock)	7, 8	2.0	1.1

¹ Apparent abiotic rate periods for subaerial disposal were weeks 12-109 and weeks 12-93 for replicates 1 and 2 respectively; for subaqueous disposal, weeks 24-205; for subaqueous disposal modified by alkaline addition, weeks 8-224 (both untreated and pretreated rock).

²Pyrrhotite oxidation rates were expressed as a function of mathematically derived pyrrhotite surface area and estimated using a specific surface areas = 0.0162 m²/g rock (units 1-6), 0.0188 m²/g rock (units 7-8) and 0.0178 m²/g rock (units 11-14), where d = 1 x 10⁻⁴ m, specific gravity = 4.6, and surface roughness factor = 1.

Figure 16. Water covers inhibited biologically-mediated sulfide mineral oxidation, but did not affect apparent abiotic oxidation rates based on cumulative sulfate release.

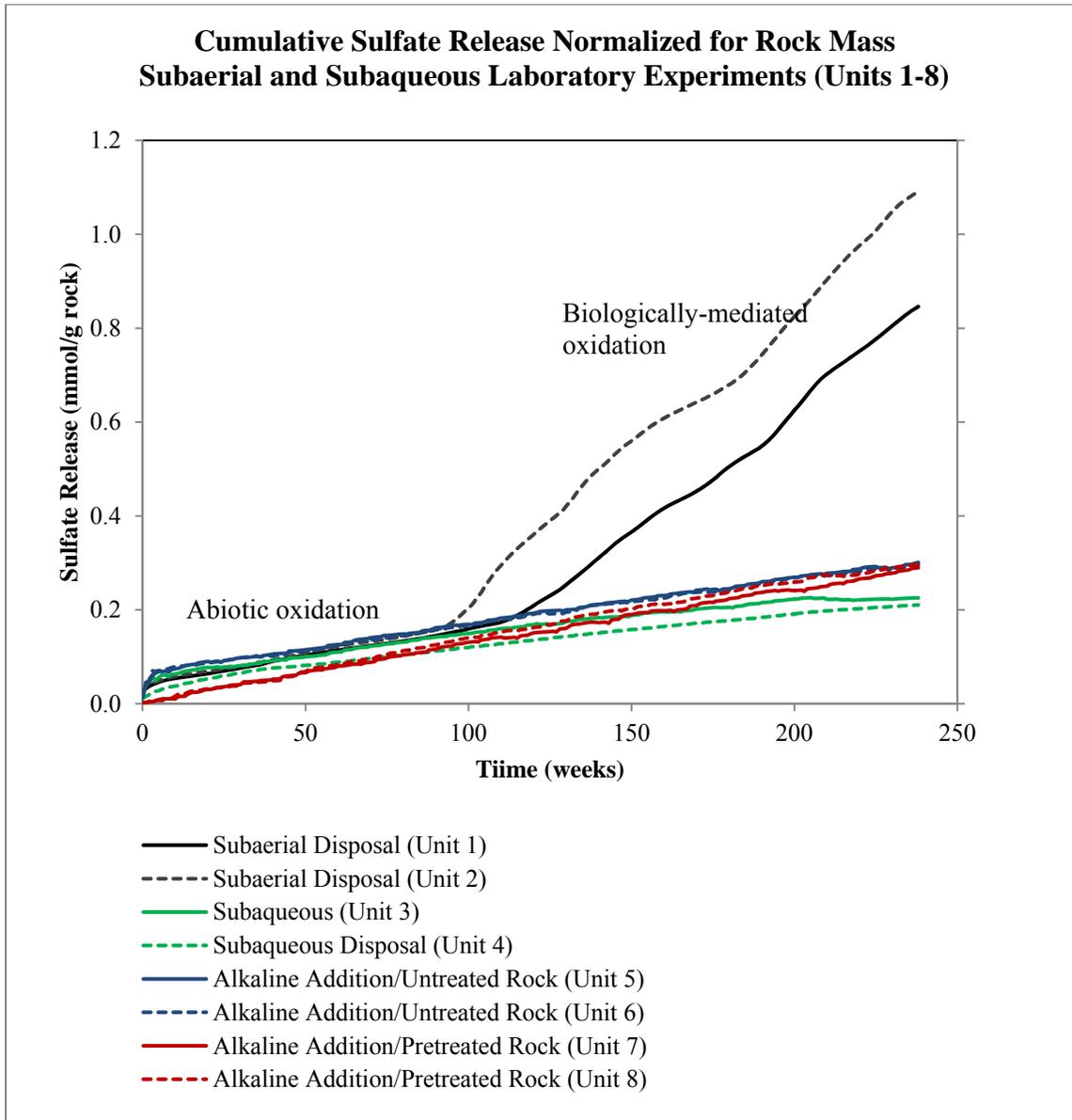


Figure 17. Less than 15% of the sulfur available in the waste rock had been released as sulfate by week 200, when sulfide oxidation rates in Units 3 & 4 decreased sharply. Similarly, sulfur depletion from the rock used in units 6 and 8 (which received alkalinity during the initial 238 and 224 weeks, respectively) was less than 25% at the time of the observed sulfide oxidation rate decrease (weeks 378 and 364, respectively).

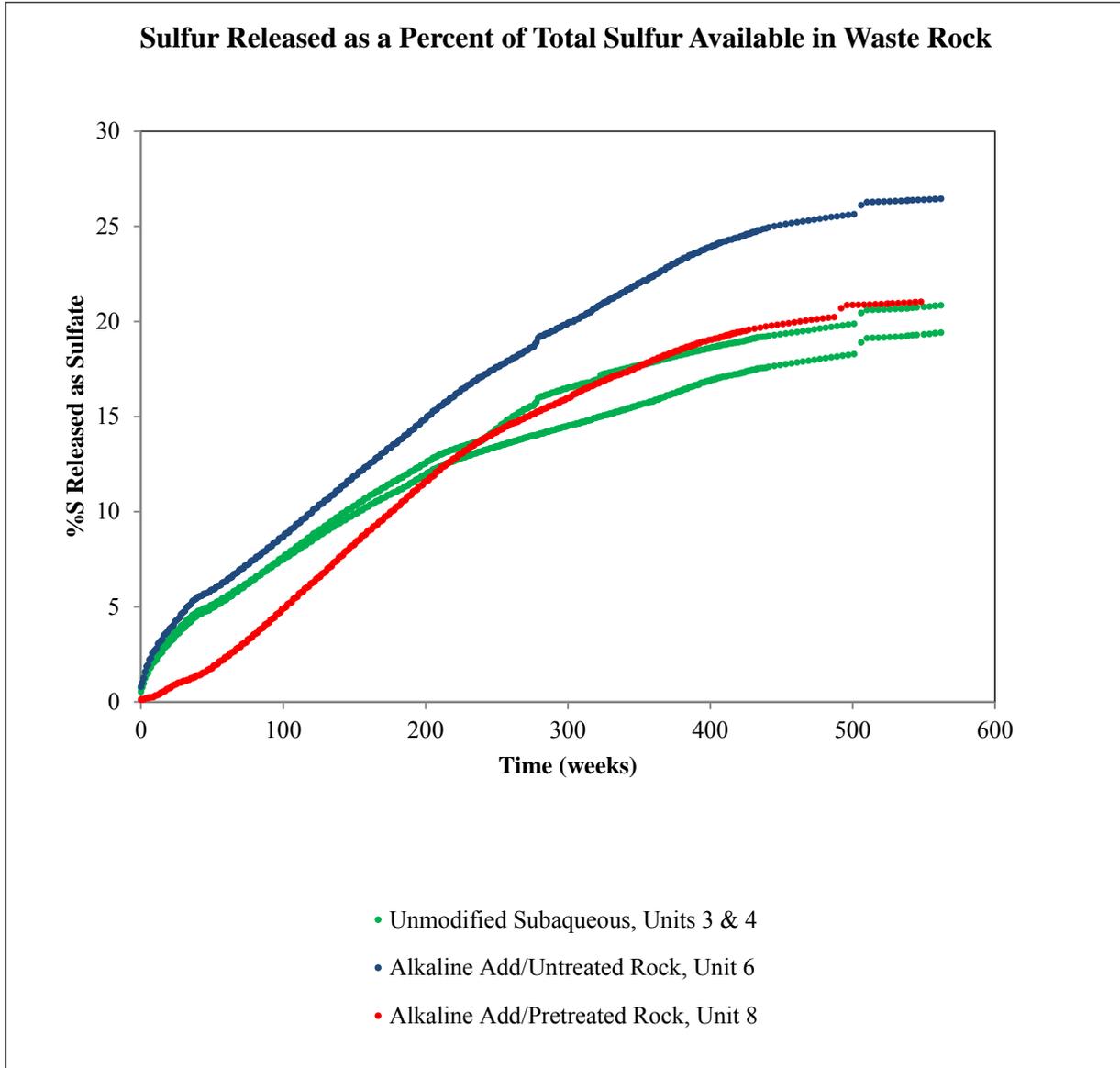
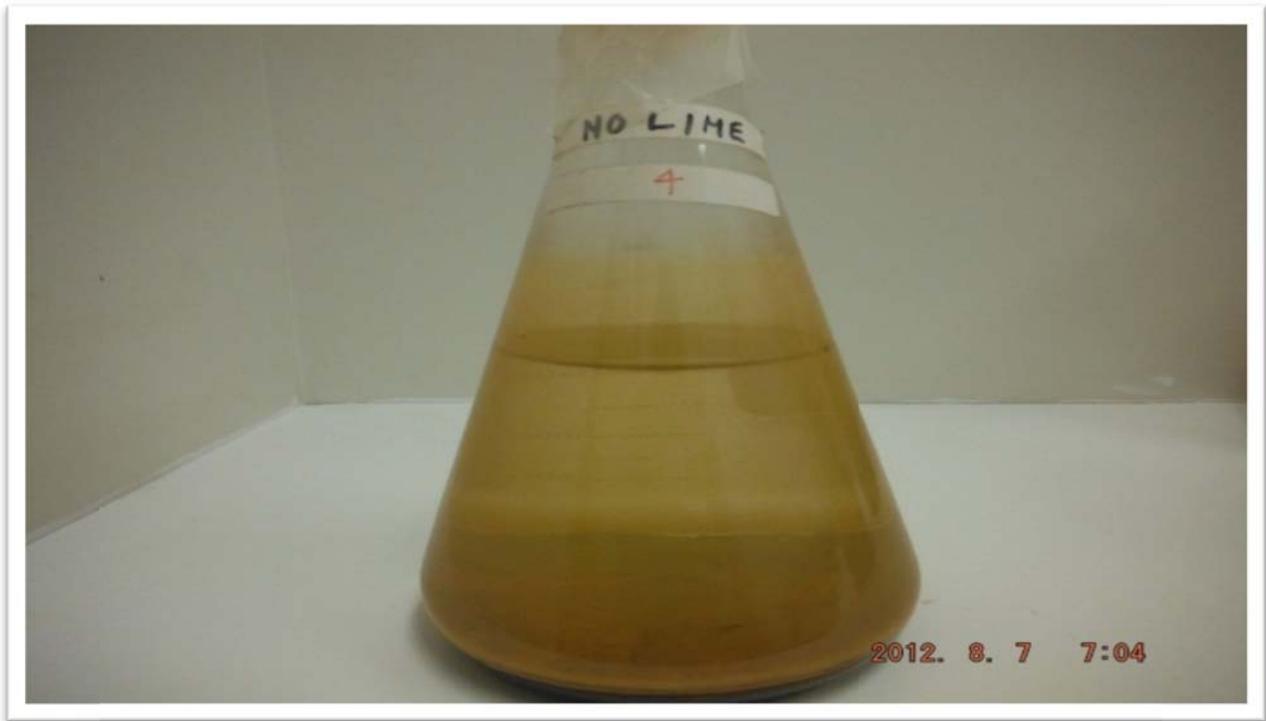


Figure 18. Rust-colored coatings were clearly visible on the Virginia hornfels rock/ water interface at the conclusion of the subaqueous disposal experiments. These coatings may have inhibited further sulfide oxidation.



6.4. Objective 4: Waste Rock Amended With an Oxygen Consuming Layer

6.4.1. Leached Waste Rock (Units 3, 5 and 7)

Addition of a composted yard waste layer to the previous subaqueous disposal simulations contributed to higher levels of cumulative sulfate release when compared to their respective controls (Figure 19). Based on the compost control results presented in section 4.6.1, approximately 0.7 mg SO₄/g rock is likely to have come from each 75-g dose of compost. An initial 15 week period of elevated sulfate release in units 3 and 5 was observed and attributed to labile forms of sulfate present in the compost. This period was prolonged to 67 weeks in unit 7 due to the application of a second dose of compost at week 58 to maintain circumneutral pH in the water cover.

In all six subaqueous simulations, the initial subaqueous sulfate release rates approximated the abiotic rates observed in the subaerial simulations (Table 22). The presence of a compost layer over the leached waste rock resulted in little difference in the rates of sulfate release when compared to their respective controls (Table 22). The only notable difference was from Unit 7 (compost amended, compare to Unit 8) during the first 59 weeks of this experiment, when sulfide oxidation increased from 2 to 3.3 nmol (kg rock·s)⁻¹ (Table 16). Subsequent to a second addition of compost, rates approximated those from the controls.

In all six simulations (compost amended and controls), sulfate release rates eventually decreased roughly 50% to the range of 0.5 – 0.8 nmol (kg rock·s)⁻¹, with most values near 0.6 nmol (kg rock·s)⁻¹ (Table 22). In Units 3 and 4 (subaqueous disposal with no additional mitigation), sulfate release rates had decreased to 0.3 nmol (kg rock·s)⁻¹ prior to the addition of compost (Table 9). After compost addition, there was no discernible difference in release rates, and therefore pyrrhotite oxidation rates, when compared to the control. This was likely due to the presence of iron oxyhydroxide coatings or similar precipitates on the waste rock prior to addition of the compost layer rather than sulfide mineral depletion (13%, Figure 20). Thus, the compost layer had no further effect on pyrrhotite oxidation in the waste rock.

Similar results were observed in Units 5 (compost) and 6 (control). The difference observed in these two corresponding units was not the magnitude of sulfate release rates, but the time periods over which those rates occurred. In the control (Unit 6), apparent pyrrhotite oxidation continued at 1.2 nmol (kg rock·s)⁻¹ for 140 weeks and then decreased to 0.6 nmol (kg rock·s)⁻¹. In the corresponding compost amended Unit 5, the expected decrease in pyrrhotite oxidation (from 1.3 to 0.8 nmol (kg rock·s)⁻¹) did not occur for 200 weeks and only 28% of the sulfide minerals depleted (Figure 20). One explanation for this result may be that organic matter in the compost sequestered iron released due to pyrrhotite oxidation before iron oxides or other iron precipitates could form. If iron was sequestered in organic complexes, formation of iron oxide coatings or precipitates at the mineral surface could be inhibited, thereby allowing sulfide mineral oxidation to continue at a constant rate.

Results from Unit 7 appeared to be somewhat anomalous in that the initial dose of compost did not buffer pH. It may be that the pH decrease created an acidic environment within the waste rock that contributed to accelerated oxidation. The second dose of compost at week 59 did increase pH to circumneutral levels. However, it is possible that this only affected the water cover above the waste and not the pore waters within the waste. In other words, an acidic microenvironment may have still existed within the waste rock pore spaces throughout this experiment. This may in part explain the elevated sulfate release rates observed in the first 70 weeks after the initial compost addition (Table 22). However, the observed oxidation rate still

exceeds the rate that would be expected for simple subaqueous disposal. Consequently, the results from Unit 7 are considered anomalous and cannot be adequately explained.

It should be noted that by the end of the period of record (562 weeks), sulfate release rates from all six subaqueous simulations converged at roughly $0.6 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, irrespective of the compost amendment. Thus, the observed decrease in sulfate release must be attributed to another mechanism such as the formation of iron oxyhydroxide coatings or precipitates, rather than the presence of an oxygen-consuming layer. Additional solid phase analyses to determine the presence, distribution and form of iron in the leached solids and compost would provide additional insight. However, these data are not presently available.

Figure 19. Examination of linear periods of sulfate release indicated little to no difference in sulfide mineral oxidation when leached waste rock was amended with compost in subaqueous disposal conditions. Approximately $0.007 \text{ mmol SO}_4/\text{g rock}$ may have been contributed by the compost itself. (Second phase of experimentation continued from the first 238 weeks, and renumbered at “week 1.”)

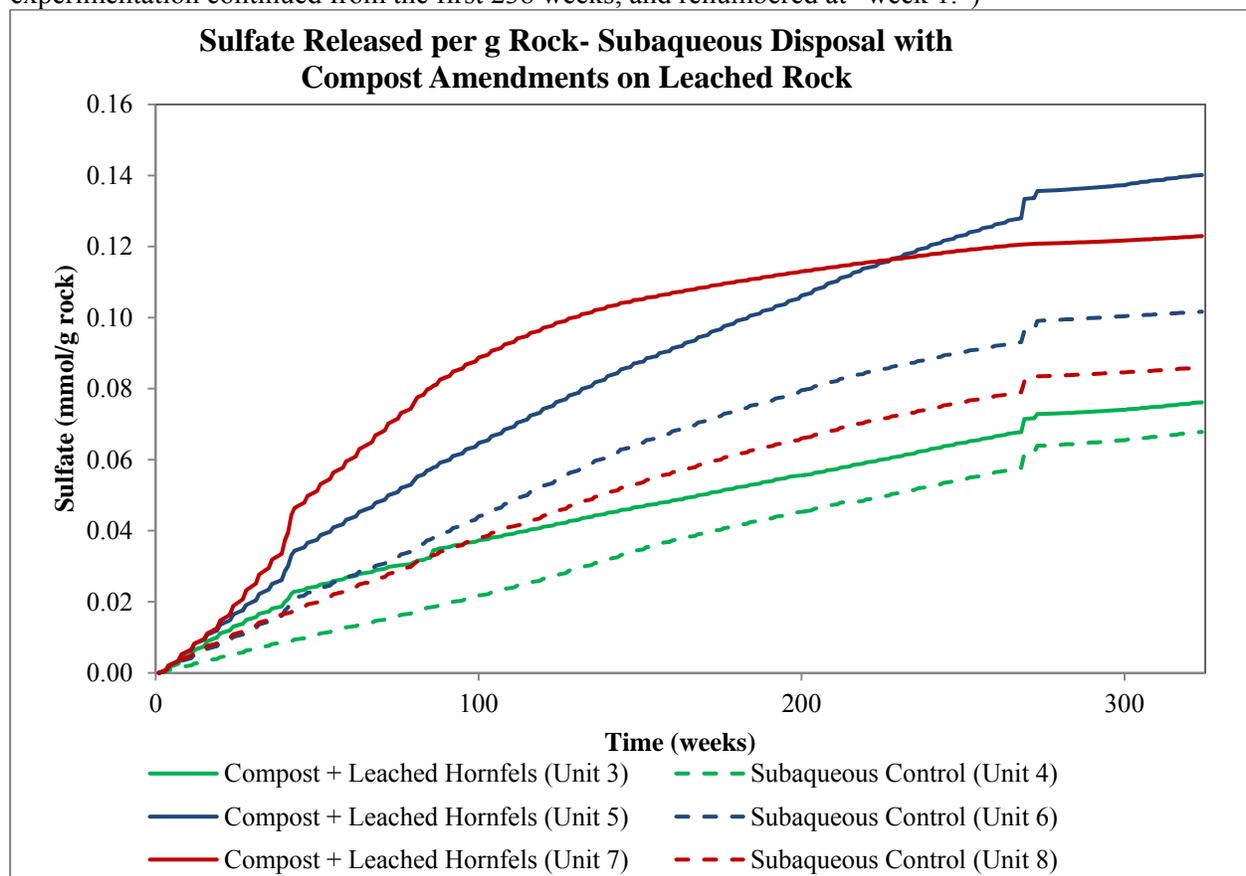


Table 22. Rates of sulfate release from subaqueous leached waste rock disposal simulations expressed in $\text{nmol (kg rock}\cdot\text{s)}^{-1}$. Compost amendment of the leached waste rock made little difference in sulfate release rates. Eventually, sulfate release rates converged on a value of $0.6 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$.

Simulation¹	Subaqueous Rate (pre-compost)	Control (no compost)²	Compost-amended³	Rate Description
Subaqueous, leached rock (Units 3 & 4)	0.3	0.6	0.6	Iron oxyhydroxide coating or precipitate
Subaqueous, alkaline addition, leached & untreated rock (Units 5 & 6)	1.7	1.2	1.3	Abiotic
		0.6	0.8	Iron oxyhydroxide coating or precipitate
Subaqueous, alkaline addition, leached & pretreated rock⁴ (Units 7 & 8)	2.0	1.1	3.3	Abiotic
		0.6	0.5	Iron oxyhydroxide coating or precipitate

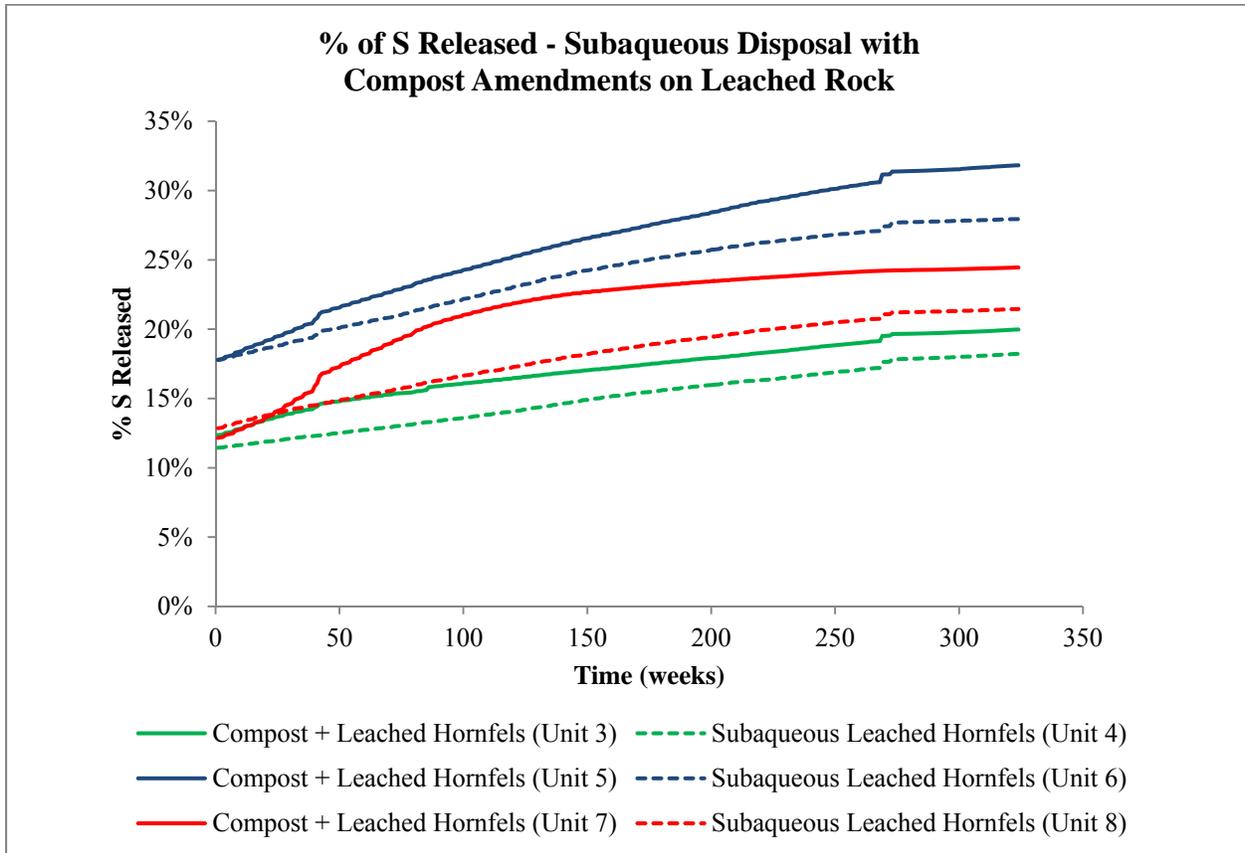
¹ Solids used in this phase of experiments was continued from the first phase of subaqueous simulations. The units were renumbered at week 1 when the compost amendment was added.

² Observed rate decreases for control units 6 and 8 took place at approximately 140 weeks after the second phase of the experiment began.

³ Observed rate decreases for units 5 and 7 took place 200 and 70 weeks, respectively, after compost had been added.

⁴ pH in this unit decreased during the first 58 weeks of testing, at which point another 75 g of compost was added.

Figure 20. Only 18 – 32 percent of sulfur available in the waste rock had been removed after 324 weeks (548 – 562 total weeks) of leaching, based on cumulative sulfate release. Consistent decreases in the rate of sulfate release that occurred between weeks 70 and 200 could not be explained by sulfur depletion (12 – 28%).



6.4.2. Fresh Waste Rock (Units 13 – 14)

As observed with the leached waste rock experiments, addition of a compost layer to fresh waste rock in a subaqueous environment resulted in a quick release of labile sulfate from the compost during the first 7 weeks (Figure 21). Between weeks 7 and 95, both the subaqueous control units and the compost-amended units replicated well. The addition of compost had little effect on the rate of sulfate release (Table 23). Initial rates of sulfate release for the waste rock controls and the compost amended units were in fairly good agreement at 1.7 and 1.5 nmol (kg rock·s)⁻¹, respectively (Table 23). Thus, compost amendments made little difference in sulfide mineral oxidation rates during the first 95 weeks of the experiment.

After 95 weeks, sulfate release rates from the subaqueous waste rock controls decreased to 0.6 nmol (kg rock·s)⁻¹. This was consistent with results from the previous laboratory experiments. However, sulfate release rates from compost amended fresh waste rock did not decrease appreciably throughout the 265 weeks of record (Table 23). Closer examination of cumulative sulfate release from the compost amended fresh rock indicated that sulfate release rates nearly doubled to 3.0 nmol (kg rock·s)⁻¹ around week 100 (Table 23). Oxidation rates should be limited by the diffusion of oxygen through the water cover to the waste rock and previous data from these experiments indicate that this rate should be in the range of 1 – 2 nmol (kg rock·s)⁻¹. Thus this period of increased sulfate release from compost amended fresh waste rock was unexpected. Based on solid phase analyses of the compost and the subaqueous compost controls, sulfate release due to the compost itself would only be expected to contribute 0.007 mmol SO₄ (g rock)⁻¹ (see section 4.6.1). This potential contribution of sulfate from the compost could account for one fourth to one third of the observed sulfate release increase. It is possible that the compost contained some form of sulfur that oxidized more slowly than observed in the compost controls (20 weeks). However no data have been generated to verify this assertion.

Subsequent to the period of elevated sulfate release around week 100, sulfate release rates decreased to 1.1 nmol (kg rock·s)⁻¹ (Table 23). Based on the observed trends noted in the unmodified subaqueous disposal and compost amended leached rock simulations, this rate would be expected to be closer to 0.6 nmol (kg rock·s)⁻¹ due to iron oxyhydroxide formation. Thus, it was concluded that the compost amendment somehow interferes with the mechanism that was observed to diminish sulfide oxidation in the previous experiments.

Visual examination of the reaction units, gypsum solubility product calculations, and basic geochemical principles led to the conclusion that the diminished sulfate release rates were likely due to the formation of precipitates or coatings at the mineral surface. Although no direct quantitative analysis had been conducted, it seemed reasonable to assume that these coatings were some form of an iron oxyhydroxide. It is possible that dissolved organic matter contributed by the compost could sequester dissolved iron released by pyrrhotite oxidation. The effect would be to render iron unavailable for iron oxyhydroxide coating formation and consequently allow sulfide mineral oxidation to continue at a constant rate. Presumably this condition would continue until all sulfide minerals were depleted from the waste rock.

Figure 21. Sulfate release (mmol/g rock) from the compost amended subaqueous fresh rock disposal simulation were initially similar to the subaqueous hornfels controls. The compost may have suppressed formation of iron oxyhydroxide coatings by sequestering iron. Solid phase analyses to determine the distribution of iron in leached solids were not conducted.

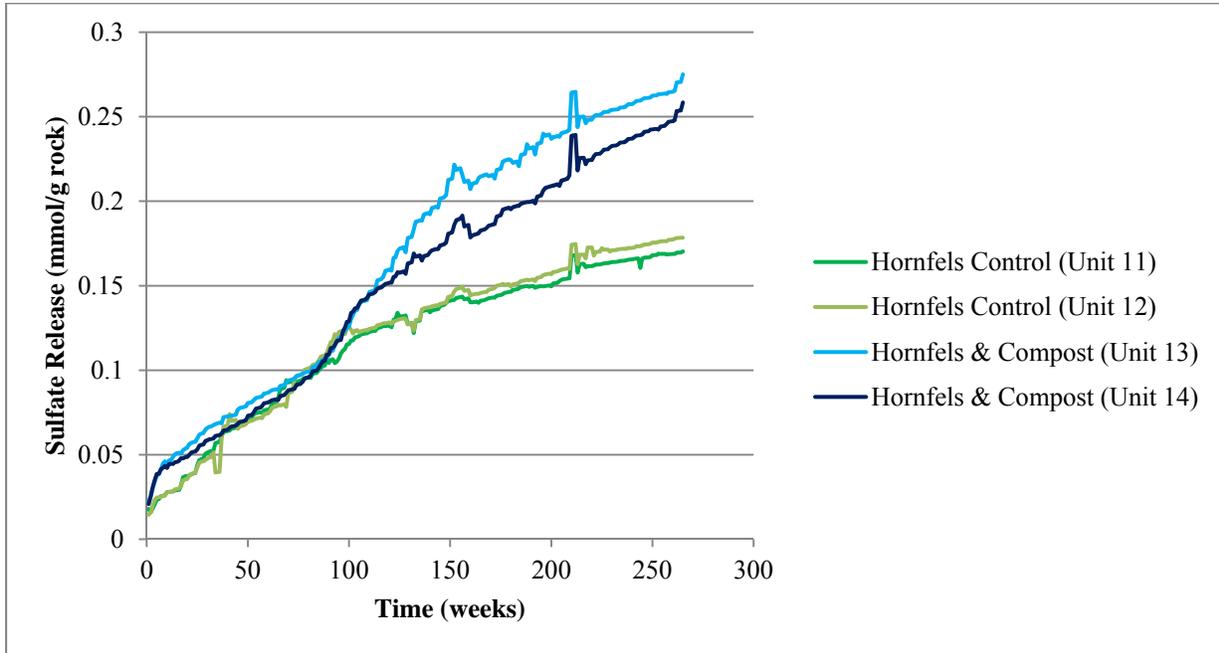


Table 23. Sulfate release rates did not follow the expected trend in the compost amended fresh waste rock simulations. No sound explanation for the apparent increase in oxidation rates that occurred around week 100 was identified. Sulfate release from the compost amended rock did not decrease toward the end of the experiment, indicating that organic matter in the compost may inhibit precipitate and/or coating formation under these conditions. Rates of sulfate release expressed in $\text{nmol} (\text{kg rock}\cdot\text{s})^{-1}$.

Approx. Weeks	No Compost	Compost-Amended
Subaqueous fresh rock units 3, 4		
20 – 200	1.3	-
200 - 238	0.3	
Compost amended fresh rock, units 11-14		
1 – 90	1.7	1.5
90- 120	0.6	3.0
120 - 265	0.6	1.1

6.5. Trace Metal Release Rates

While trace metal release rates were not the main focus of this work, it is of concern for sulfidic mine waste disposal situations. Therefore, a limited number of trace metal samples were analyzed throughout these experiments. Trace metal release rates were only calculated for the initial phase of subaqueous experiments, when the sampling frequency was monthly. Furthermore, trace metal concentrations were frequently at or below detection limits and estimated to be half the detection limits. These estimated values were used in determining release rates, which are noted with a “<” in their respective tables (Tables 10, 12 and 14). Consequently, those rates should be considered an upper limit to the possible release rate under those specified conditions.

Water covers in these waste rock disposal simulations were effective in reducing the release of trace metals such as copper, nickel, cobalt, and zinc. Trace metal concentrations were generally low, and occasionally below detection limits. In order to calculate release rates, trace metal concentrations that were below detection were estimated at one half the reported detection limit. For the subaerial disposal simulations, where drainage pH dropped sharply to 2.5 around week 100, copper and zinc release increased by factors of 40 and 7, respectively (Table 24). In contrast, nickel and cobalt release rates decreased over the same time period. Inspection of the cumulative mass release of these metals indicated that roughly 95% of nickel and 50% of cobalt present in the rock had been depleted. Thus, the decreased release rates were likely due to depletion of nickel- and cobalt-bearing minerals due to oxidation.

Trace metal release rates were reasonably steady over the course of the subaqueous experiments and appeared to respond to small changes in water cover pH. For example, copper release in the unmodified subaqueous simulation increased from 0.0004 to 0.002 nmol (kg rock·s)⁻¹ as the pH approached 3. This rate is roughly two to three percent of that observed in the subaerial simulation. Overall, trace metal release from subaqueous waste rock disposal simulations ranged from one to three orders of magnitude lower than subaerial conditions indicating that water covers do inhibit trace metal release (Table 24). However, a decrease in pH due to acid production will result in elevated trace metal release as seen in the subaqueous condition without alkaline addition.

Table 24. Trace metal release rates (in nmol (kg rock·s)⁻¹) from Virginia hornfels waste rock in subaqueous environments were one to three orders of magnitude lower than in the subaerial simulations. “<” indicates that this rate was determined using estimated values and should be considered an upper limit to release rates.

Simulation	Approximate pH Range	Cu	Ni	Co	Zn
Subaerial Disposal Initial	3.5	0.002	0.1	0.01	0.01
Subaerial Disposal Final	2.5	0.08	0.02	0.003	0.07
Subaqueous (no alkaline addition)	3-3.5	0.0006	0.0004	<0.00006	0.005
Subaqueous Modified by Alkaline Addition	6.5-7.5	<0.00003	<0.0003	<0.00003	<0.00006
Pretreated Subaqueous Modified by Alkaline Addition	6.5-7.5	<0.00003	0.0006	<0.00005	<0.00005

7. Summary and Conclusions

To assess management options for sulfide-bearing Minnesota waste rock, experiments were conducted for four to six years on Virginia Formation hornfels rock containing 12 - 14 weight percent pyrrhotite ($\text{Fe}_{0.9}\text{S}$). These experiments examined the mitigative potential of 1) subaqueous disposal (238-week period of record); 2) subaqueous disposal augmented by addition of alkalinity to the water cover (230 weeks); and 3) incorporation of an oxygen consuming compost layer at the water/rock interface of mine waste disposed under water (324 weeks with leached solids from aforementioned experiment; 265 weeks with fresh solids). Thin layers of rock (~11 mm) were used in the subaqueous settings to more precisely reflect reaction rates at the water-rock interface and variation of these rates over time.

Under subaerial conditions (562 weeks, simulating disposal on the land surface), drainage pH was in the approximate range of 3.7 to 4 for the first 100 weeks, declined to near 3 over a 20-week period, then slowly declined to near 2.5 after 200 weeks. During the first 100 weeks sulfate release rates averaged roughly $2 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$, and sulfide mineral oxidation was assumed to proceed abiotically. Concurrent with the pH decrease, the rate increased to $9.5 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ and biological mediation was the likely cause of the rate increase. This accelerated rate of sulfide oxidation persisted through roughly week 300 and subsequently decreased due to sulfur depletion in the waste rock. Following the pH decline near week 100, rates of copper and zinc release increased by factors of 30 and 7, respectively. In contrast, rates of nickel and cobalt release decreased by factors of 10 and 2, respectively.

Water covers effectively limited the oxidation rate of pyrrhotite present in the thin layers of subaqueous Virginia hornfels rock. Initial pyrrhotite oxidation rates in the subaqueous disposal environment approximated those observed for the abiotic oxidation period in the subaerial environment. All three subaqueous alternatives resulted in similar initial rates of sulfate release, approximately $1 \text{ to } 2 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$. Removing residual soluble components from the rock surface prior to immersion, adding alkalinity to the overlying water, or introducing compost provided no further reduction in oxidation rates.

Use of a thin layer of rock allowed determination of temporal variations in oxidation rates in the subaqueous setting. Whereas the initial subaqueous rates were similar to those during the abiotic period of the subaerial simulation (prior to week 100), the subaqueous conditions did not yield the more rapid rates indicative of biological mediation under the subaerial conditions. Furthermore, relative to the subaerial environment, sulfate release rates in the subaqueous environments decreased after a lesser degree of sulfide mineral depletion. Sulfate release decreased to roughly $0.6 \text{ nmol (kg rock}\cdot\text{s)}^{-1}$ after roughly 200 – 400 weeks of reaction. For the subaerial simulation this decrease occurred at approximately 300 weeks, when sulfur depletion was in the range of 70 – 100%. In contrast, sulfur depletion ranged from 6 – 13 % at the time sulfide oxidation rates from the unmodified subaqueous simulations decreased (100 – 200 weeks; units 3, 4, 11 and 12).

For the units that received alkalinity to maintain pH (Units 6 and 8), sulfide oxidation rates did not decrease until 140 weeks after alkalinity additions ceased, which resulted in nearly twice as much sulfur depletion (23 and 16 %, respectively) from the rock. Visual evidence of rust-colored coatings on mineral surfaces and SEM evidence from similar Duluth Complex rock indicated that the formation of iron oxyhydroxides was likely. The presence of these iron oxyhydroxides, either as coatings at the rock-water interface or as alteration shells at the mineral surface, could inhibit oxygen transport, and consequently, pyrrhotite oxidation.

The addition of a layer of composted yard waste did not decrease sulfide oxidation rates. The decrease in oxidation rates observed after 200 – 300 weeks in the unamended subaqueous simulations was not observed in the compost amended simulations using fresh rock. It is speculated that organic matter in the compost may sequester iron released from minerals such as pyrrhotite, inhibiting the formation of iron oxyhydroxide coatings at the sulfide mineral surface. This would then allow sulfide mineral oxidation to continue at a constant rate rather than decrease due to oxygen transport limitations across the coating boundary.

While not the primary focus of these experiments, trace metal release is a concern when considering disposal of Virginia formation waste rocks. Copper, nickel, cobalt and zinc release rates for the subaerial environment were approximately ten to one hundred times those for the subaqueous setting. The subaqueous rates did respond to changes in water cover pH, with the lowest release rates at circumneutral pH. Trace metal release rates were not determined for subaqueous compost amended simulations.

Results from these laboratory subaqueous disposal simulations have important implications for a full-scale subaqueous disposal scenario when compared to subaerial disposal. First, biologically mediated subaerial oxidation rates were approximately five times higher than the abiotic rates observed in the subaqueous simulations. Second, since oxygen can penetrate to a substantial depth in the rock mass (possibly the entire rock mass) in a subaerial setting, the total release of acid and other solutes would increase for a larger rock mass disposed on the land's surface. In a subaqueous environment, oxygen transport, and therefore oxidation, deep within a rock bed would become negligible. Third, the formation of iron oxyhydroxides believed to have formed after several years of dissolution would be expected to further reduce the mass of solute release due to sulfide mineral oxidation under subaqueous conditions.

The rates of acid generation for subaqueous conditions must be considered to ensure that acid conditions would not develop in a pit upon disposal of pyrrhotite-bearing mine wastes. The potential for residual acid salts on the mine wastes prior to disposal must also be taken into account. The neutralization required for the acid inputs can then be quantified. Sources of neutralization include alkaline water inputs to the pit, dissolution of alkaline components in the pit walls, and of alkaline amendments. Furthermore, the release of trace metals from sulfide minerals into neutral waters must be assessed.

8. Acknowledgments

Solid-phase chemical and mineralogical analyses were conducted by Don Schnortz of Lerch Brothers (Hibbing, MN) and Louis Mattson of Midland Research (Nashwauk, MN), respectively. The dissolution experiments were conducted by Kathleen Willis and Pat Geiselman under the direction of David Antonson. Sulfate was analyzed by Jean Matthew, while calcium and magnesium were analyzed by Albert Klaysmat at the Hibbing office of the Minnesota Department of Natural Resources. Jon Wagner and Anne Jagunich were responsible for data management as well as production of tables and figures for this publication. Funding for this report and laboratory work since July 2011 was provided by Minerals Cooperative Environmental Research and Iron Ore Cooperative Research state funding plus industry match. Funding for laboratory work prior to July 2011 was provided by State general fund.

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