

TESTING DURABILITY OF ACID ROCK PASSIVATION TO ROOT SYSTEM ACTIVITY WITHIN GREENHOUSE COLUMNS¹

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Abstract: The durability of a potassium permanganate protective coating (passivation) on potentially acidic waste rock was examined for preventing acid generation. There is limited biological and physical data on the environmental impact and durability of passivation technology. The objective was to determine if exposure of passivated acid waste rock to repeated cycles of intensive root growth would affect coating stability. Passivated treatments were compared to limed waste rock in columns with and without plants. Passivation stability was determined by measuring the pH, electrical conductivity (EC), iron, and sulfate of drainage leachate and saturated paste extracts by the use of a hydrogen peroxide stability test. The treatments were kept at field capacity and were leached once a month with reverse osmosis (RO) water. The stability study showed 1) no root system effects on passivation stability: and 2) no difference in expression of potential acidity of waste rock between passivation and adding lime at the rate of 15% (by weight) to the waste rock.

Additional Key Words: sulfidic rock, acidity, root growth, acid mine drainage, potassium permanganate protective coating, hydrogen peroxide stability test

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Introduction

The Gilt Edge Gold Mine is an open pit heap leach mine located in the northern Black Hills near Lead, South Dakota. The waste rock from the mining operation is acid generating, due to the presence of pyrite FeS_2 which oxidizes when exposed to oxygen and water resulting in the release of H_2SO_4 and associated heavy metals. Release of these contaminants from the waste rock can potentially affect local water supplies and the cold-water fisheries (EPA, 2006). Strawberry Creek and Bear Butte Creek, in particular, are at risk from contamination from Cu, Cd and Zn at the Gilt Edge Mine (EPA, 2006). If the Gilt Edge Gold Mine is left unreclaimed, the water supplies and wells in the area could potentially be impacted by acid, heavy metals, and sulfate.

Pyrite oxidation is a significant problem in rehabilitation of former gold mines (Groves, 1974). When pyrite is brought to the surface, the pyrite is exposed to the elements (oxygen and water) and oxidation with subsequent generation of sulfuric acid occurs (Kohnke, 1950). Arsenic, Se, and other heavy metals are easily solubilized by the acid and made available for release into the environment (Boon, 1986). Once the H_2SO_4 is formed, other heavy metals are solubilized from the waste rock and migrate into leachates that end up in the water resources (Kohnke, 1950). A water resource that contains a pH 3.5 or less would be toxic to biological life (Kohnke, 1950).

Different remediation techniques have been tried over the years for treating acidic drainage. The most common method for treatment of acidic drainage from mines is by addition of lime, which neutralizes the acid and precipitate metals as metal oxides. The resulting neutralized waste rock can improve the chances of sustaining plant growth (Boon, 1986). However even with an addition of 125% lime (based on acid-base forming materials) to acid generating rock, acid generation can still occur (Doolittle and Hossner, 1997).

This study examined the durability of a potassium permanganate passivation of sulfide containing waste rock compared with a lime treatment. The objective of this study was to evaluate the effect of intensive plant root growth of on the stability of a potassium permanganate coating on sulfide bearing waste rock as compared to a calcium carbonate.

Methods

Passivation

The procedure used for passivation was adapted from a method used for high wall rock at the Golden Sunlight Mine in Montana (Glenn Miller, Personal Communication, 2004). At the Golden Sunlight Mine, the passivation method was applied at large scale to the surface of the highwall with a triple-nozzle spray system (McCloskey, 2005) while at South Dakota State University was applied as lab scale. Waste rock at South Dakota State University was mixed with a solution consisting of 0.2 gram/litter (g/L) NaOH, 0.7 g/L $\text{Ca}(\text{OH})_2$, 1 g/L MgO and water to raise the waste rock pH to >12. The basic solution was decanted and discarded. The pH-adjusted waste rock was then mixed with a potassium permanganate solution. Because the amount of chemicals required for the pH adjustment and passivation depended on the acidity and surface area of the rock, the initial protocol was modified by exposing the waste rock to a concentrated potassium permanganate solution such that pH was maintained >12 for 3 hours. After the passivation treatment, the solutions were decanted and the passivated waste rock was

washed with tap water to remove excess salts. The procedure deposits a coating on the surfaces of acid generating minerals armoring them from oxidative attack.

Liming

The original waste rock (WR1) as analyzed by South Dakota State University was low in sulfur (S) and low in acid generating material. A second, high S and high acid generating waste rock (WR2) was created for this project by combining 15% high S overburden from the Gilt Edge Mine with 85% WR1. Portions of both materials were limed with 15% CaCO₃ (by weight) to create limed low sulfur waste rock (LLSWR) and limed high sulfur waste rock (LHSWR). The waste rock mixtures (limed and non-limed) were mixed using a cement mixer.

Hydrogen Peroxide (H₂O₂) Passivation Test

The hydrogen peroxide (H₂O₂) passivation test determines whether the acid generating waste rock (AGWR) is passivated and is a variation of a standard passivation peroxide test (Glenn Miller, Personal Communication, 2004). Larger-sized samples were used, due to the heterogeneity of the waste rock samples. Two hundred-fifty mL of deionized water was added to 40g of AGWR, the mixture was mixed and pH which was then determined. Acid samples were titrated with 0.1 N NaOH to a pH of 8.5. Alkaline samples were titrated to a pH 8.5 with 0.1 N H₂SO₄. The amounts of acid or base that were added to the solution were recorded. Then 50 mL of 35% H₂O₂ was added and the time was recorded. The pH was checked every 5-10 minutes for the first 30 minutes, every 15-30 minutes for the next hour, and each hour thereafter for a period of six hours. If the pH was ≤ 5 during the 6-hour period, the sample was considered to be actively generating acid. If the sample remained pH ≥ 5 for this time period, the sample was considered to be protected from acid generation. The original waste rock had a pH 4.58 after 6 hours.

Greenhouse Setup

There were four experimental treatments (passivated high acid [PHAWR], passivated low acid [PLAWR], limed high acid [LHAWR], and limed low acid waste rock [LLAWR]) with a total of 144 experimental units. Each treatment was split into a plant and a no-plant subtreatment with two repetitions. Each column (experimental unit) consisted of 10.2 cm (4 in) polyvinylchloride (PVC) drainpipe cut into 33.0 cm (13 in) sections with a cap at the lower end of the PVC pipe. The cap had a central drainage hole fitted with a tubing connector to facilitate leachate collection. On the top of the PVC pipe, a coupling was placed to aid in the holding of water during leaching tests. The columns were placed in wooden racks and held upright. Each rack contained four columns. There were 36 columns in each treatment, 18 columns containing plants and 18 columns containing no plants (control section). Each column was packed with 22.9 cm (9 in) of a waste rock treatment. Approximately, 2.5 cm (1 in) of Vienna topsoil (Fine-loamy, mixed, superactive, frigid Calcic Hapludolls) was mixed into the top 2.5 cm (1 in) of the waste rock and an additional 5.1 cm (2 in) of Vienna topsoil was placed on top. Each column had 5 mL (1 tsp.) of osmocote (fertilizer 17 N – 7 P – 12 K) added. Throughout the growing season a fertilizer solution (15 N – 30N -15K) was added to sustain plant growth. The columns were leached with 1200 mL deionized water (DI) corresponding to one pore volume of the soil (40% porosity). Pore volume was estimated for the columns by multiplying the drainable porosity and column volume. Drainable porosity was determined by the displacement of the 1 L of waste rock packed to a similar density as found in the columns and subtracted this from 1 L. The leachate was collected for analysis. Immediately following the first leaching, *Sorghum bicolor* (forage sorghum) was planted in half of the columns. Every 30 days for the next year,

the columns were leached with 600mL of DI water. Beginning in the second month, two columns, one plant and one no-plant treatment were removed from the experiment. After the third month, columns were removed for analysis every 60 days. After the forage sorghum had matured, the plants were harvested and the plant material dried and saved. Subsequent “crops” were planted and harvested in the following sequence, *Triticum aestivum* L. (spring wheat), *Pisum sativum* L. (forage peas) twice, and *Sorghum vulgare* Pers. (forage sorghum).

Data Collection

Leachates were collected and analyzed for pH, electrical conductivity (EC), iron (Fe) and sulfate (SO_4^{2-}).

The columns were divided into four zones. Vienna topsoil; Zone 1 a mixture of Vienna topsoil plus the waste rock, Zone 2 upper waste rock; and Zone 3 lower waste rock (Fig. 1).

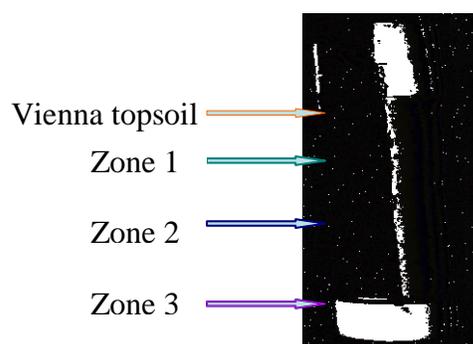


Figure 1. Zones of soil divided in the column.

Soil pH, EC, iron, and sulfates were determined (Thomas, 1996; Roades, 1996; Loeppert and Inskeep, 1996; Tabatabai, 1996). The water extract was analyzed to determine pH and EC. Iron concentrations in leachates were determined by atomic adsorption (Loeppert and Inskeep, 1996). Sulfates were analyzed colorimetrically (Tabatabai, 1996). Samples were tested for passivation failure using the H_2O passivation test whenever columns were removed for soil analysis. The data for the original low acid waste rock was pH 3.7, EC $700 \mu\text{s cm}^{-1}$, sulfate 321 mg kg^{-1} , and iron 0.14 mg kg^{-1} , and for the original high acid waste rock was pH 3.2, EC $985 \mu\text{s cm}^{-1}$, SO_4 907 mg kg^{-1} , and Fe 6.70 mg kg^{-1} .

Analysis of variance were run using the GLM Proc of Systat Version II. The study was designed and analyzed using a complete random design. The mean comparisons were done using an F restricted less significant difference (LSD).

Results and Discussion

Leachates

Leachate from columns with and without plants had lower sulfate concentrations over time, presumably a result of leaching of the sulfate and dissolution of remaining gypsum, CaSO_4 (Fig 2). There were no significant differences between the remediation treatment or added high acid waste rock treatment in terms of the reducing sulfate and iron concentrations. The original low acid waste rock had sulfate 321 mg kg^{-1} and original high acid waste rock sulfate 907 mg kg^{-1} . Sulfate concentrations in the leachate significantly decreased with increasing number of days. From day 240 through day 338, the sulfate losses leveled off. No significant

differences were observed between the plant and no-plant columns for most leaching. At day, 94 sulfate concentrations were higher in the no-plant system while at day 122-212 they were slightly higher in the plant systems.

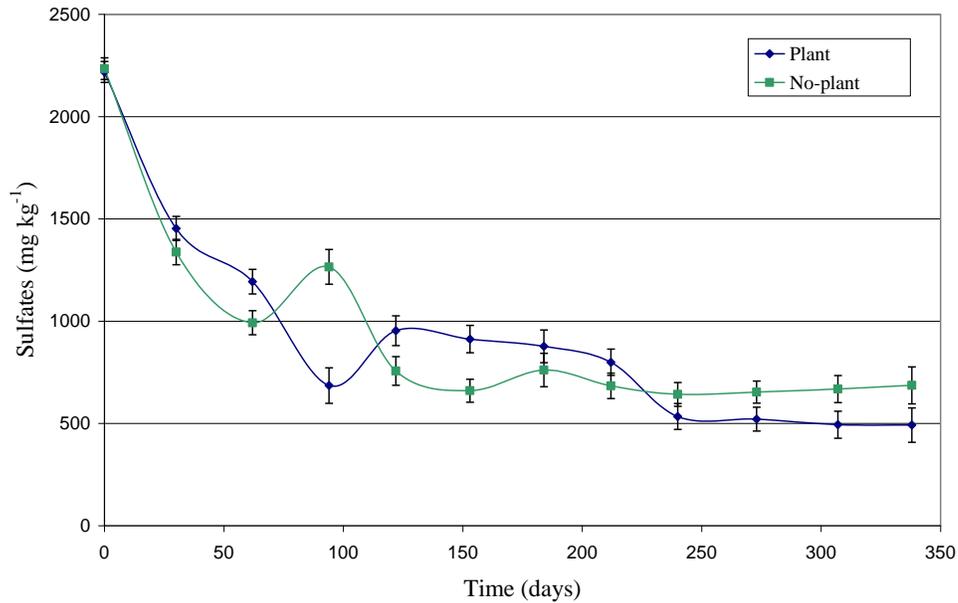


Figure 2. Effect of intensive plant root growth of sulfate concentration on column leachate sulfate. Error bars repeat standard error of the mean for each reading period.

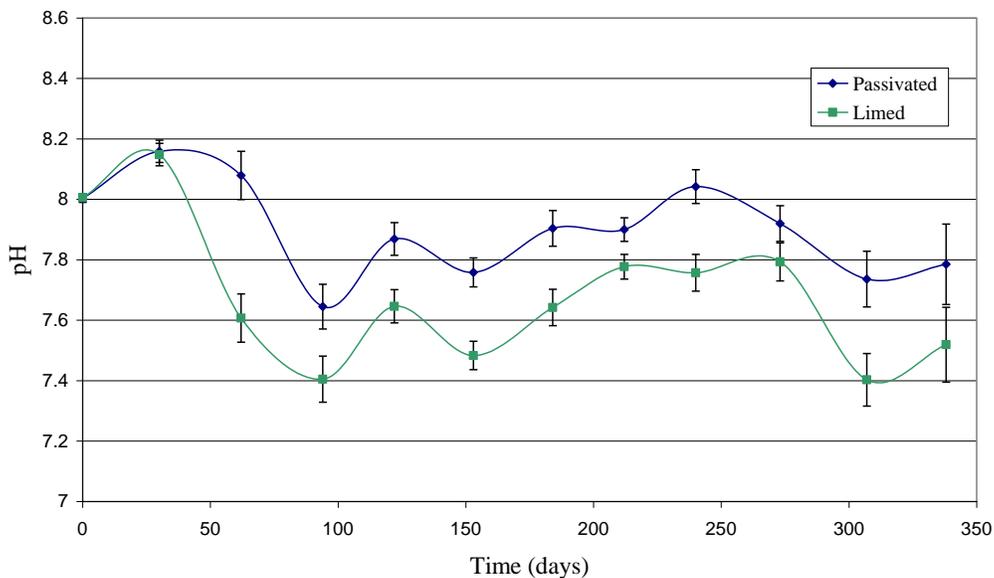


Figure 3. Remediation treatment effects on pH of column leachate. Error bars repeat standard error of the mean for each reading period.

The passivation treatment resulted in higher leachate pH throughout the study compared to the limed treatment (Fig. 3). Initially the pH of the leachate was similar for both remediation treatments. Both remediation treatments reduced pH of the leachate during the course of the study by less than 0.5 pH units. The original low acid waste rock had pH 3.7 and original high acid waste rock pH 3.2. The limed treatment had a lower pH (average 7.7) than the passivated treatment pH (average 7.9) after 30 days of the study. The other treatments (plant and acid waste rock) were not significantly different from the control.

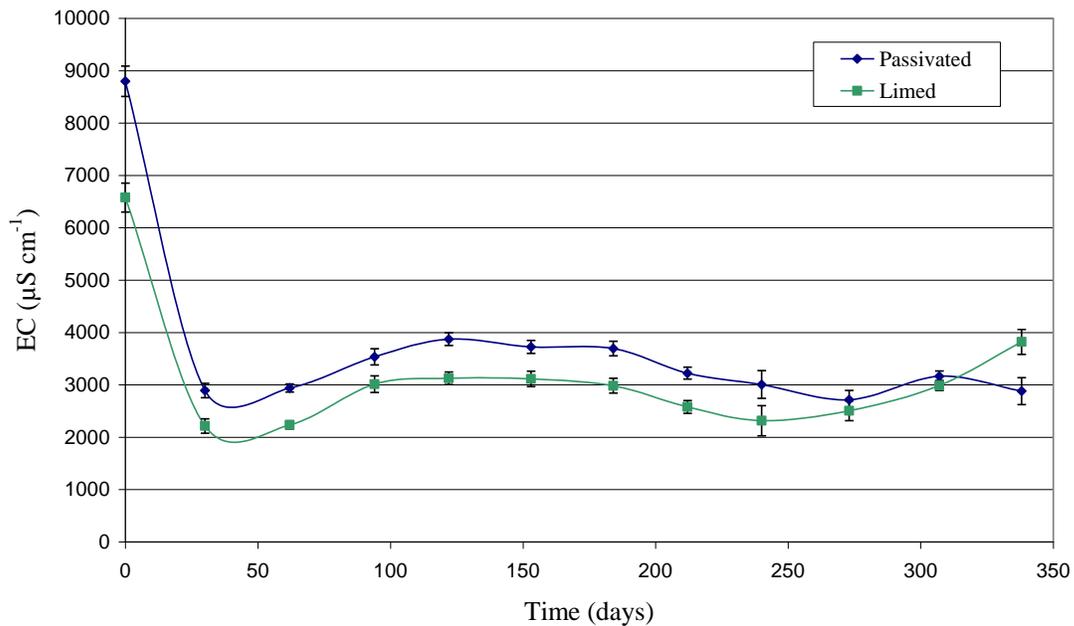


Figure 4. Effect of limed and passivated treatments on leachate electrical conductivity (EC). Error bars repeat standard error of the mean for each reading period.

Leachate electrical conductivity (EC) for passivated and limed treatments showed similar trends compared to pH (Fig. 4). Leachate EC values were significantly higher at time zero than at other times during the study. The original low acid waste rock had EC $700 \mu\text{S cm}^{-1}$ and original high acid waste rock EC $985 \mu\text{S cm}^{-1}$. The passivated treatment exhibited higher EC values throughout the study until day 338 when EC values in the limed treatment increased. There was no plant treatment interaction with remediation treatment. However, total average EC values were lower in the plant columns ($1806 \mu\text{S cm}^{-1}$) than the average no-plant columns ($4296 \mu\text{S cm}^{-1}$) after 30 days of the study. This was most likely due to nutrient/salt uptake by the plant root system. Throughout the study, all treatments received fertilizer to obtain optimum plant growth. Both plant and no-plant columns were treated similarly.

Waste rock

There were no pH differences between remediation treatments and of the soil depth zones. From the initial measurement of soil pH on zone 1 to the last soil pH measurement, there was a significant decrease in soil pH (Fig. 5). Plant high acid (PHA) and plant low acid (PLA)

remained similar in soil pH throughout the study. A similar trend was observed in zone 2 except that the reduction in pH was less for NPLA than in zone 1 (Fig. 6). In zone 3, there was no effect of treatment on pH over time (Fig. 7). Figure 7 shows a pH >5 and the H₂O₂ passivation test showed a similar trend with the remediation treatments remaining at pH >5.

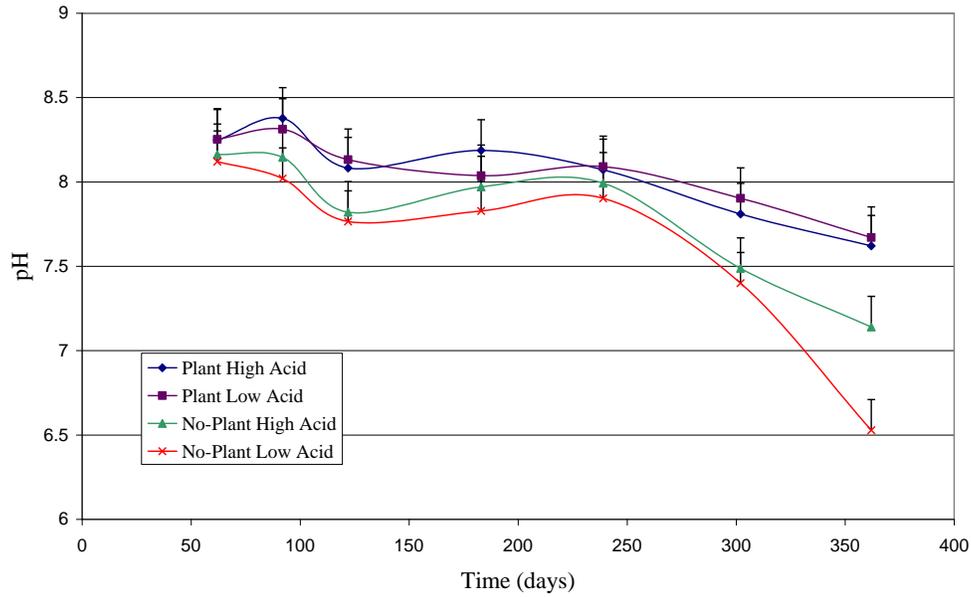


Figure 5. Soil pH of Zone 1 overtime, for plant and added waste rock treatments. Error bars repeat standard error of the mean for each reading period.

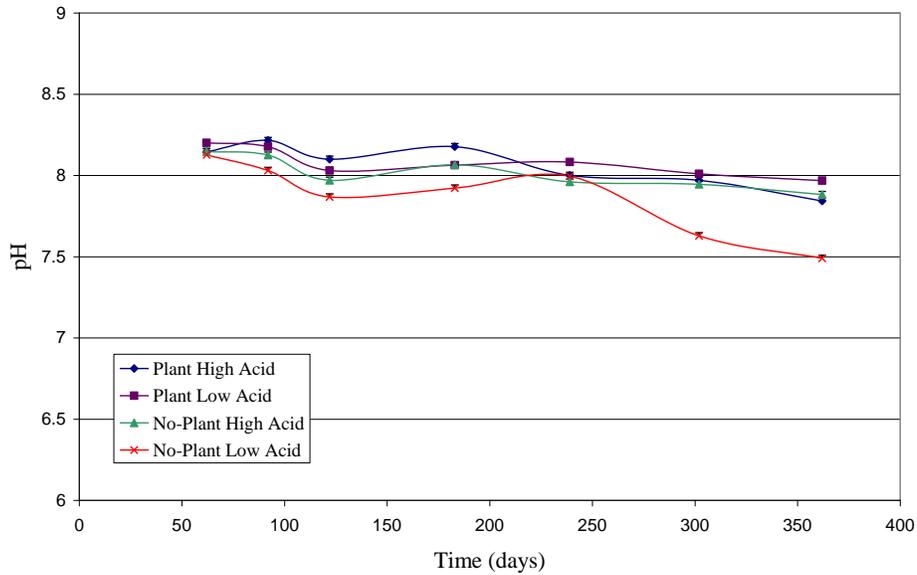


Figure 6. Soil pH of Zone 2 overtime for plant and added waste rock treatments. Error bars repeat standard error of the mean for each reading period.

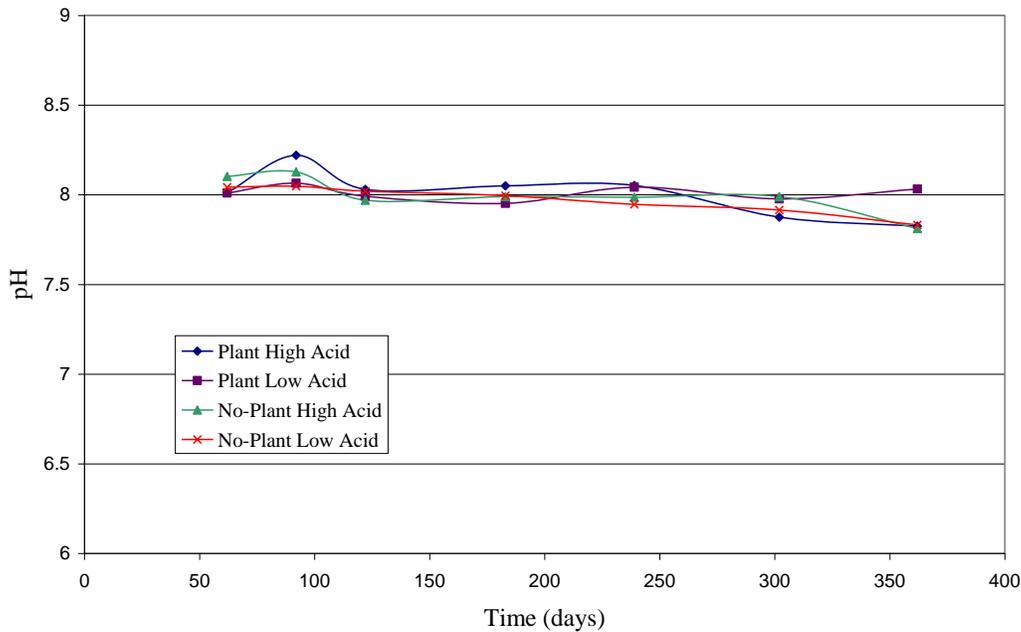


Figure 7. Soil pH of Zone 3 overtime for plant and added acid waste rock treatments. Error bars repeat standard error of the mean for each reading period.

The effect of remediation treatment on soil EC and soil sulfates tend to follow each other as seen in Tables 1 and 2. There was a significant interaction between remediation and acid waste rock addition treatments. The high levels of soil EC for zone 1 were likely higher than zone 2 and 3 due to the addition of fertilizer. There were no significant changes in EC or soil sulfate concentrations with time. The high level of soil EC for the passivated high and low acid is believed to be due to the passivation process. The passivation process added additional salts to the waste rock. The higher sulfate concentrations found in zones of the passivated low acid waste rock treatment could be do to variability of waste rock and of application treatment. The opposite relationship was observed in the limed treatment and can be explained by the higher sulfate content of the higher acid waste rocks.

Table 1. Soil electrical conductivity (EC) from passivated, limed, high acid and low acid generating waste rock.

Waste Rock Treatment	Acid	Zone 1	Zone 2	Zone3
		-----	$\mu\text{S cm}^{-1}$	-----
Passivated	High	1169	674	948
Passivated	Low	1154	912	1418
Limed	High	1336	1213	1739
Limed	Low	1161	451	603
	LSD _{0.05}	NS	408	777

Table 2. Soil sulfate concentration from passivated, limed, high and low acid generating waste rock.

Waste Rock Treatment	Acid	Zone 1	Zone 2	Zone 3
		-----	mg kg ⁻¹	-----
Passivated	High	314	244	433
Passivated	Low	303	454	804
Limed	High	430	563	1004
Limed	Low	319	170	259
	LSD _{0.05}	NS	187	NS

Conclusion

Intensive root growth was established for the passivated and limed treatments. Plant roots did not appear to affect the passivation coating, which might have caused lower pH, higher EC and sulfates, and failure of the remediation treatments in the H₂O₂ passivation test. A release of potential acidity would result in a high level of concentrations of sulfates in Zone 1-3 which was not observed. Leachate pH was relatively high for the passivation and liming treatments, which would result in low mobility of heavy metals.

Fertilizer affected soil pH in the PHA, PLA, NPHA and NPLA treatments. The NPHA and NPLA seemed overall to have a lower pH than the PHA and PLA. The addition of fertilizer was taken up by the plants in the plant treatments (PHA and PLA) but there was nothing to remove the fertilizer in the no-plant treatments (NPHA and NPLA). The plants used in this study produced aggressive and intensive root growth. The roots had little effect on the breakdown of the passivation treatment or lime treatment. The final pH reading remained substantially above greater than 5.

The passivation treatment and liming treatment used in this study resulted in no breakdown of iron sulfides and acid generation. The passivation and liming treatments gave similar results on both waste rock and soil materials containing both high and low levels of acid waste rock. Passivation and liming treatments resulted in significantly higher soil pH compared to untreated waste rock measured at the beginning of the study.

For future study, several improvements should include 1) higher acid bearing waste rock; 2) include columns of untreated waste rock; 3) longer testing period; and 4) treat waste rock with organic acids in the column treatments

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