

254 CONTAMINANT MIGRATION FROM ACIDIC-METALLIFEROUS TAILINGS INTO AN *IN-SITU* LIME AMENDED ROOT ZONE DURING A SEVEN YEAR PERIOD¹

D. J. Dollhopf*, and J. D. Goering

Abstract. Concern exists that acidic (pH 2.2), metalliferous (Cu, Fe, Zn) and As laden tailings treated *in-situ* with lime will in time become chemically unsuitable for plant growth. Specifically, acidity and metals from untreated tailings may migrate upward into the lime amended tailings via mechanisms associated with mass flow of water or diffusion. In spring 1995, a demonstration area was constructed where the 0-60 cm tailings zone, having a clay loam texture, was amended with a combination of CaCO₃ and CaO to facilitate contaminant precipitation from solution and a pH suitable for plant growth (pH 7.0-8.0). No water table was present within 6 m of the reclaimed surface. During the subsequent seven year period, the semiarid site supported grass production consisting of several wheat grass species and wildrye. Following sampling in 6 mm depth increments in replicated test pits, it was determined that after seven years as much as 7 cm of the amended zone nearest the acidic tailings had acidified (pH 4.0-4.5). Similarly, the specific conductance in this acidified zone increased significantly (9.8-12.3 dS/m) compared to that in amended tailings nearer to the surface (2.4-3.0 dS/m). Neither As, Cu, Fe nor Zn were present at significantly greater concentrations in the acidified zone, indicating these elements did not migrate from acidic tailings into the lime amended zone. It was not known whether acidification of the lime amended zone nearest the tailing was at equilibrium or not, suggesting additional acidification of the amended zone in the future was possible. These results indicate acidic-metalliferous tailings treated with *in-situ* liming methodologies should account for upward migration of acidity during the design process.

Introduction

Historical mining and ore processing in southwest Montana resulted in the presence of large volumes of waste and contaminated soils covering approximately 800 square kilometers (USEPA and Montana Department of Environmental Quality, 1998). The U.S. EPA placed this area on

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²Douglas J. Dollhopf, Professor, and John D. Goering, Geologist, Reclamation Research Unit, Department of Land Resources and Environmental Sciences, Montana State University, Proceedings America Society of Mining and Reclamation, 2003 pp 254-265

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the National Priorities List and site remediation is governed by the "Superfund" program. One feature of this area is the 1,300 hectare Opportunity tailings impoundment which contains 100 million m³ of fine grained ore processing waste having an acidic pH (2.2) and high concentrations of metals (Cu and Zn) and As. In order to reestablish a grassland on this impoundment a 45 cm thick cover must be constructed that will remain suitable for plant growth in perpetuity (USEPA and Montana Department of Environmental Quality, 1998). In this regard, the Record of Decision requires either 1) lime must be used to amend the acidic nature of these tailing within the 0 - 45 cm depth increment, or 2) lime must be used to amend the 0 - 30 cm increment of tailings and an additional 15 cm of cover soil applied on top of the amended tailings.

Concern exists that lime-amended tailings that overlie acidic-metaliferous tailings will in time become entirely, or in part, chemically unsuitable for plant growth. Specifically, acidity and metals from tailings may translocate upward into cover soil via mechanisms associated with mass flow of water or diffusion.

Seven years ago in 1995, a demonstration area was constructed where 60 cm of tailings were amended with lime (RRU 1997). This treated area continues to support plant growth seven years following construction and provided an excellent opportunity to determine whether the lime-amended zone had deteriorated due to the upward translocation metals and acidity.

The objective of this investigation was to quantify the degree (if any) to which *in-situ*, lime amended tailings (0 - 60 cm) have degraded during a seven-year period due to upward migration of acid, salts, or contaminants (As, Cu, Fe, and Zn).

Methods And Site Characteristics

In 1995, the lime requirement to neutralize both active and potential acidity in the 0.14 ha tailings demonstration area was determined using a modified Sobek method (Sobek et al. 1978, RRU et al. 1987) and the SMP buffer method (ASA 1982, method 12-3). Analytical results were applied to Equation 1 (where the mass (Mg) is conventionally expressed in short tons, but the terms are Mg/Mg and can be expressed as t/t or be unit-less) to calculate the total lime requirement.

$$\text{Mg CaCO}_3 / 1000 \text{ Mg soil} = (\% \text{ HNO}_3 \text{ extractable S} + \% \text{ Residual S}) 31.25 + 23.44 (\% \text{ HCl extractable S}) + \text{SMP Lime Requirement, Mg CaCO}_3 / 1000 \text{ Mg soil} \quad (1)$$

Both CaO and CaCO₃ were applied according to the application rate based on calcium carbonate equivalence (CCE) (ASA 1965, method 91-4.2), percent of oversize (> 0.25 mm) particles determined by dry sieving, and gravimetric water content. A total of 90 Mg CaO/ha and 230 Mg CaCO₃ /ha were applied and incorporated into the 0 - 46 cm tailings depth increment with a BOMAG MPH 100 rotary mixer. Due to an inherent tailings swell factor, the amended zone had a final thickness of 60 cm. In addition, 530 Mg/ha black-vitreous slag was applied and incorporated into the 0 - 15 cm depth increment. Lastly, 120 m³/ha compost were incorporated into the 0 - 7.5 cm tailings depth increment with an agricultural rototiller.

In May 1995, the site was seeded to a mixture of 5 species of wheatgrass (*Agropyron dasystachyum*, *A. elongatum*, *A. intermedium*, and *A. trichophorum*), 3 species of wildrye (*Elymus cinereus*, *E. giganteus*, and *E. junceus*), fescue (*Festuca ovina*), birdsfoot trefoil (*Lotus corniculatus*) alfalfa (*Medicago sativa*), and 8 native forbs. By the second growing season the site was composed almost entirely of perennial grasses having a 36.2 % cover and a production of 2610 kg/ha (dry weight). Average annual precipitation is 34.7 cm, with one-third received during May and June.

Tailings deposition into the impoundment occurred during the period 1940 to 1980. The average slope of the impoundment surface is 1 %. Tailings thickness beneath the demonstration area is approximately 15 m. Within the demonstration area, the 0-1 m depth increment of tailings is dominated by a silty clay loam texture and 7 % rock content. Since 1995, these tailings have been well drained and no gravitational water was observed to a depth of 6 m.

Three pits were excavated during the summer of 2002 at random positions across the demonstration area exposing the amended and unamended tailings profile. Each pit was precisely sampled in twelve depth increments which included eight samples, each of 6.4 mm depth, centered on the amended/unamended interface; three equal depth samples of the entire amended profile above the 6.4 mm samples; and one 76 mm depth increment of unamended tailings below the 6.4 mm samples (Figure 1). Samples were analyzed for total metals (Cu, Fe, and Zn) and As using x-ray fluorescence (Ashe Analytics 1995), pH and specific conductance from saturated paste extract (ASA 1965,

method 62-1.3.2.1), and CCE. Particle size distribution was estimated by the hand texture method.

Tailings Pond Surface

Limed Tailings with Slag	<div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 0 auto;">Mean depth increments for three test pits</div> 0 - 19.38 cm
Limed Tailings	19.38 - 38.76 cm
Limed Tailings	38.76 - 58.42 cm
Limed Tailings	58.42 - 59.06cm
Limed Tailings	59.06 - 59.69 cm
Limed Tailings	59.69 - 60.33 cm
Limed Tailings	60.33 - 60.96cm
Unamended Tailings	60.96 - 61.60 cm
Unamended Tailings	61.60 - 62.23 cm
Unamended Tailings	62.23 - 62.87 cm
Unamended Tailings	62.87 - 63.50 cm
Unamended Tailings	63.50 - 71.12 cm

Figure 1. Mean sampling depths for profiles composed of *in-situ* treated tailings and unamended tailings at a impoundment in southwest Montana.

Quality control samples including field and laboratory splits, standards and cross contamination

blanks were collected in order to calculate analytical accuracy, precision, and representativeness. An audit of all data determined analytical results were within control standards set forth by PTI Environmental Services (1992).

A two-way analysis of variance test was applied to these data sets. In all cases, data sets either had a normal distribution or were numerically transformed to attain a normal distribution prior to applying analysis of variance. All data sets passed the equal variance test. If significant differences were detected between means at the 0.05 probability level, the Student-Newman-Keuls method was used to determine which means were different from each other (Snedecor and Cochran, 1973).

Upward Migration Of Contaminants

The basal 2.5 cm thick layer (58.4 - 61.0 cm) of amended tailings had a significantly lower pH (3.99-4.52) compared to the pH (6.83-7.07) in amended tailings nearer to the surface (Table 1). This indicates hydrogen ions from unamended tailings deeper than the 60.96 cm depth migrated upward and acidified a portion of the amended zone. The pH in this acidified layer is sufficiently low to impair plant root development. The thickness of this impacted zone was easily observed in the field test pits (Figure 2). Given the three test pits, the acidified layer thickness was 0, 3.8, and 7.6 cm thick. Table 1 only shows the 58.4 -61.0 cm thick layer was acidified since the bulk of the 38.8 - 58.4 cm depth increment was non-impacted lime amended tailings which resulted in neutralization of the acidified portion of that sample during sample mixing/preparation in the analytical laboratory.

Similarly, the basal 2.5 cm thick layer (58.4 - 61.0 cm) of amended tailings had a significantly greater specific conductance (9853-12317 dS/m) compared to that in amended tailings nearer to the surface (2450-3073 dS/m) (Table 1). This may have been due to the lower pH and associated production of soluble chemical products from weathering of pyrite minerals in these tailings. The specific conductance in the acidified layer is sufficiently high to impair plant root development.

The CCE indicated some residual CaCO_3 (1.2-1.6 %) remained in the acidified tailings zone (Table 1). Since available CaCO_3 should have been consumed during the upward migration of hydrogen into the acidified zone, it is presumed the CaCO_3 present is unavailable for chemical reaction. This may be due to large amendment particle size or chemical encapsulation phenomena (Evangelou, 1995).

Total metal and arsenic concentrations in the 0-19.4 cm depth increment were significantly greater compared to all tailings increments at greater depth (Table 2). This was due to incorporation of black-vitreous slag in the 0-15 cm depth increment. The slag had high concentrations of metals

Table 1. Chemical characteristics for *in-situ* treated tailings on Opportunity Pond D2.

Mean Depth Increment (cm)	Interval Description	pH ¹ (su)	Specific Conductance ² (dS/m)	Calcium Carbonate Equivalence ³ (%)
0 - 19.38	Limed Tailings with Slag	6.8 a [‡]	2460 a	6.4 a
19.38 -38.76	Limed Tailings	6.9 a	2450 a	0.8 b
38.76 - 58.42	Limed Tailings	7.1 a	3070 a	1.4 b
58.42 - 59.06	Limed Tailings	4.5 b	9850 ab	1.2 b
59.06 - 59.69	Limed Tailings	4.3 bc	10500 abc	1.6 b
59.69 - 60.33	Limed Tailings	4.2 bc	11400 bcd	1.5 b
60.33 - 60.96	Limed Tailings	4.0 bc	12300 bcd	1.4 b
60.96 - 61.60	Tailings	3.0 bc	15000 bcde	
61.60 - 62.23	Tailings	2.1 c	16000 bcde	
62.23 - 62.87	Tailings	2.1 c	18000 cde	
62.87 - 63.50	Tailings	2.1 c	19400 de	
63.50 - 71.12	Tailings	2.0 c	20800 e	

¹ The [H⁺] value was transformed using the -log₁₀ function. Normality and equal variance tests were passed. Two-way ANOVA was used. Power of the test = 1.0.

² Normality and equal variance tests passed. Two-way ANOVA used. Power of the test = 1.0.

³ The % CCE for unamended tailings was not determined in the laboratory. Normality and equal variance tests passed. Two-way ANOVA used. Power of the test 0.98.

‡ Means (n=3) followed by the same letter in the same column are not significantly different, P = 0.05.

(As, Cu, Fe, Zn, and others). Total iron concentrations in the three 6.4 mm depth increments at the base of the amended zone (mean of 51800 mg/kg) were significantly greater than 38.76-58.42 cm tailings increment (35200 mg/kg) located nearer to the surface. This indicated iron from the unamended zone may have migrated upward into the amended tailings. Total concentrations of As,

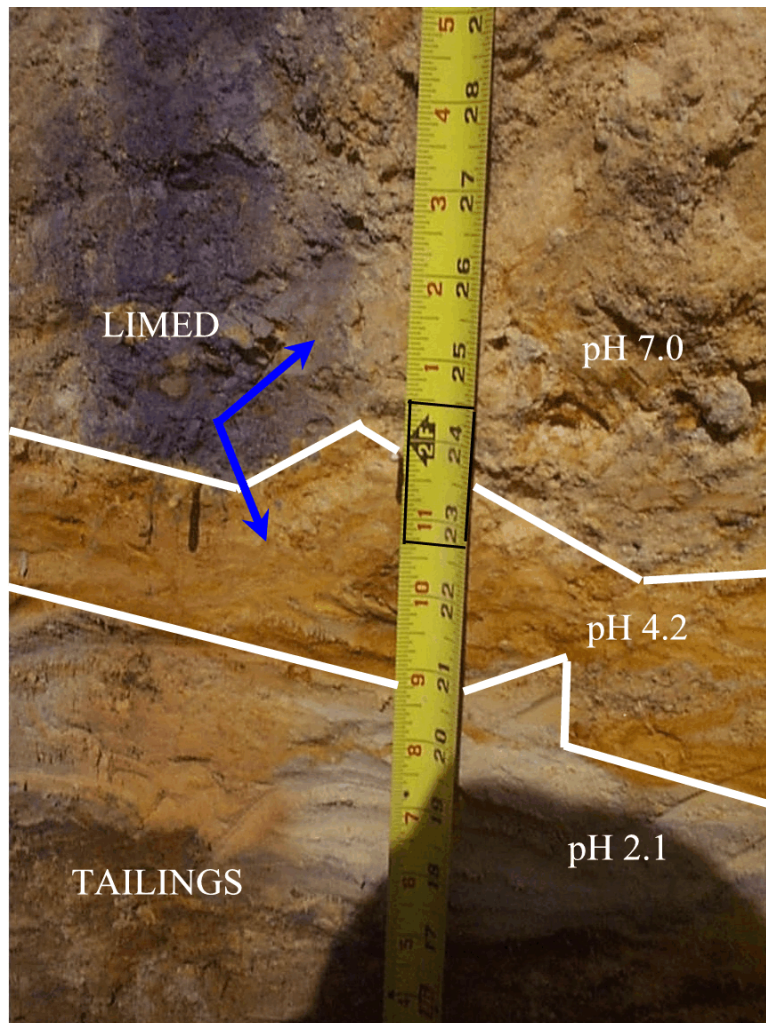


Figure 2. Photo acidified tailings profile seven years

previously. Portion of profile left of the tape was treated with lime exhibiting portion of a treated with lime pH indicator, which indicates a purple/blue zone greater than pH 7 and yellow zone generally less than pH 4.

Cu and Zn were not significantly different across depth increments sampled in the amended zone below the depth of incorporated slag. This indicated these elements did not migrate from unamended tailings upward into the lime amended zone.

Possible Mechanisms Causing Upward Migration

The hydrogen ion concentration gradient from unamended tailings (pH 2.3) to lime amended tailings (pH 6.9) was approximately 4.7×10^{-3} moles/l H^+ to 1.2×10^{-7} m/l H^+ . This equates to a gradient of nearly 40,000 : 1. For total As, Cu and Zn the concentration gradient from unamended tailings to lime amended tailings was approximately 1:1. Data for water soluble contaminants (determined in 1996) indicate the concentration gradient was approximately 340:1 for As (III) (2255 to 6.6 $\mu\text{g/l}$), 3970:1 for Cu (273666 to 69 $\mu\text{g/l}$), 7580:1 for Fe (541830 to 72 $\mu\text{g/l}$), and 2630:1 for Zn (272300 to 104 $\mu\text{g/l}$) from unamended tailings to amended tailings (RRU 1997). Resident H^+ in the unamended tailings solution could have migrated upward in response to the large concentration gradient by diffusion mechanisms. During a portion of the year the tailings profile may have remained moist due to spring precipitation, and during periods when there was no water movement, H^+ ions may have diffused upward via the water continuum through the tailings matrix and up into the amended tailings. Apparently the smaller concentration gradient, and perhaps lower inherent mobility, for As, Cu, Fe and Zn resulted in little, if any, migration of these elements into the amended tailings zone. During the period November 1995 through September 1996, the tailings profile water balance was measured in this demonstration area (RRU 1997). Precipitation during this period (27.8 cm) was somewhat below the long term average (34.7 cm). Site specific calibrated heat dissipation sensors used to measure the soil water matric potential indicated no precipitation percolated down through the interface, located at the 60 cm depth, that separated lime amended and unamended tailings. Therefore, during the 11 month period of monitoring, no chemical products were leached from amended tailings into the unamended tailings. The water balance analysis indicated that during the months of May, July and September evapotranspiration exceeded precipitation. Therefore, during these three months it was less likely that precipitation and subsequent percolation approached the amended-unamended tailings interface, and the opportunity for H^+ to move up into the amended zone by mass flow of water was greater. During other months of the monitored period, precipitation

exceeded evapotranspiration. Thus the opportunity was greater for water to approach the amended-unamended tailings interface, which may have helped keep upward migration of H⁺ from encroaching

Table 2. Chemical characteristics for *in-situ* treated tailing on Opportunity Pond D2.

Depth Increment (cm)	Interval Description	Arsenic ¹	Copper ²	Iron ³	Zinc ⁴
		(mg/kg)			
0 - 19.38	Limed + Slag	1420 a [‡]	2250 a	114000 a	8040 a
19.38 - 38.76	Limed	208 b	684 b	40200 ef	606 b
38.76 - 58.42	Limed	171 b	843 b	35200 f	1130 b
58.42 - 59.06	Limed	280 b	1210 b	44600 ef	815 b
59.06 - 59.69	Limed	335 bc	1050 b	48500 de	729 b
59.69 - 60.33	Limed	364 bc	903 b	51200 cde	627 b
60.33 - 60.96	Limed	452 bc	717 b	55700 bcde	654 b
60.96 - 61.60	Tailings	699 c	912 b	78000 abc	824 b
61.60 - 62.23	Tailings	669 c	1060 b	74600 ab	921 b
62.23 - 62.87	Tailings	464 bc	944 b	69300 abc	923 b
62.87 - 63.50	Tailings	393 bc	858 b	68400 abc	871 b
63.50 - 71.12	Tailings	179 b	546 b	40900 ef	653 b

¹ Normality and equal variance tests passed. Two-way ANOVA used. Power of the test for depths = 1.0.

² Normality and equal variance tests passed. Two-way ANOVA used. Power of the test = 0.84.

³ Normality and equal variance tests passed using a reciprocal data transformation. Two-way ANOVA used. Power of the test 1.0.

⁴ Normality and equal variance tests passed. Two-way ANOVA used. Power of the test 1.0.

[‡] Means (n=3) followed by the same letter in the same column are not significantly different, P = 0.05.

well up into the amended zone, and may have provided an opportunity for limited leaching of H⁺ and

water soluble metals from the amended profile.

Conclusion

In-situ treatment of tailings with lime has inherent risk that contaminants may migrate upward in the future and impair plant growth. Contaminant transport models used to predict translocation of chemical constituents from waste into cover soil often do not provide the level of assurance needed to confidently institute impoundment closure projects. Case history observations and measurements of impoundment closures using *in-situ* treatment methods become invaluable as chemical equilibrium begins to stabilize in the constructed profile over time.

After seven years, acidity (H^+) from acidic-metalliferous tailings migrated up into an *in-situ* lime-amended tailings zone as much as 7.6 cm, causing a pH 4 condition that was not suitable for plant growth. Future investigation work at this site will determine whether observed upward migration of H^+ has stabilized or whether it will impair additional portions of the *in-situ* treated tailings zone. The conclusions presented herein are those of the authors and may not represent those of the Atlantic Richfield Company (ARCO) or the Agencies involved in this investigation.

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