CONTAMINANT MIGRATION FROM ACIDIC-METALLIFEROUS TAILINGS INTO AN EARTHEN COVER DURING A 26 YEAR TIME PERIOD[1]

by

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Abstract. Concern exists that coversoil placed over acidic-metalliferous tailings will in time become chemically unsuitable for plant growth. Specifically, acidity and metals from tailings may translocate upward into coversoil via mechanisms associated with water mass flow or diffusion. Concern exists that construction of a lime layer between tailings and coversoil will not entirely impede this upward translocation of contaminants, or any impedance value may be negligible in time as the lime neutralization capacity is consumed by acidity. In 1974, 10 ha of a 330 ha tailings impoundment was covered with a 8 cm thick lime layer and topped with 41 cm of coversoil near Anaconda, MT. These acidic tailings (pH 2.1) contained enriched levels of copper, zinc and other metals. Following soil profile sampling in replicated test pits, it was determined that after 26 years no metals from tailings migrated into either the lime layer or the coversoil. The 0.7 mm thick lime unit nearest to the tailings had a decreased calcium carbonate equivalence which equated to a loss of 53 tons $CaCO_3$/ha. This decrease was attributed to upward migration of acidity from tailings into the lime layer during a brief period following construction of the earthen cover, as opposed to a steady-state process during the 26-year period. These results indicate acid from tailings has potential to migrate upward into earthen covers, but this phenomenon may be confined to a relatively thin layer at the base of the earthen cover.

Additional Key Words: tailings impoundment, acid drainage, metal contaminants

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. The U.S. EPA placed this area on the National Priorities List and site remediation is governed by the "Superfund" program. One feature of this area is the 330 hectare Anaconda tailings impoundment which contains a substrate of fine grained ore processing waste having an acidic pH (2.2) and high concentrations of metals (Cu, Zn) and arsenic. In order to reestablish a grassland on this impoundment, it was determined that a 46-centimeter soil cover was required (ARCO, 2000). Coversoil will be attained from adjacent uncontaminated geologic stratum.

Concern exists that coversoil placed over 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 coversoil via mechanisms associated with mass flow of water or diffusion. Inclusion of a lime layer between coversoil and tailings may impede upward translocation of contaminants. However, concern exists that a lime layer will not entirely impede this upward translocation of contaminants, or any impedance value will be negligible in time as the lime neutralization capacity is consumed by acidity. These concerns lead to consideration for more expensive designs that preclude translocation of solute across the coversoil - tailings interface, such as a geotextile barrier, to insure plant growth is sustained into the distant future.

In addition, if a lime layer between acidic-metalliferous tailings and coversoil is both technically and cost feasible, then design criteria pertaining to the required thickness is presently not known to preclude upward translocation of contaminants for centuries of time.

Fortunately, 26 years ago a demonstration area was constructed where both a lime layer and coversoil was

placed over these tailings. As reported by Schafer & Associates (1986), on a several hectare area of tailings the Anaconda Company placed approximately an 8 cm thickness of reject lime and 41 cm of coversoil in 1974. This demonstration area provided an excellent opportunity to determine whether either the lime layer or coversoil had deteriorated due to the upward translocation metals and acidity.

In this paper information is presented on the translocation of metals, arsenic and acidity from tailings to coversoil, and whether or not a lime layer served prevent upward migration of contaminants into the plant root zone.

Methods And Site Characteristics

In 1974 the demonstration area was seeded to *Agropyron cristatum, Bromus inermis, Elymus hispidus,* and *Onobrychis viciafolia.* In 2000, plant cover was dominated by wheatgrass and rye grass species and was considered sufficient for the intended land use. Average annual precipitation is 34.7 cm, with one-third received during May and June. Tailings deposition into the impoundment occurred during the period 1943 to 1980. The coversoil demonstration area underwent a brief period of drainage prior to 1974 to facilitate construction and was allowed to drain from that time forward, although adjacent portions of the impoundment were still in use for tailings disposal. The average slope of the impoundment surface is 1%.

Tailings thickness beneath the demonstration area was approximately 25 m. Within the demonstration area, the 0-1 m depth increment of tailings was dominated by a sandy loam texture but contained one to several thin layers (2-5 cm thick) of silty clay referred to as slimes. During 2000, this 1 m thick zone of tailings beneath the coversoil remained well drained. Plant roots were abundant throughout the 41 cm thick coversoil unit and absent from the 8 cm thick lime reject layer and underlying tailings.

Lime reject is a product produced from the calcining of limestone, which is largely CaO, but was rejected because some $CaCO_3$ failed to lose CO_2, creating a quality control issue. Thus this lime reject would have been discarded, and may have been mixed with ash produced from fuels used to heat the kiln.

Three pits were excavated at random positions across the coversoil demonstration area. In coversoil, the zone nearest to the underlying lime was sampled in approximately 0.5 cm increments for a distance of 1.5 cm, and then in 15 cm increments to the surface (Figure 1). These thin units sampled near to the lime layer were intended to detect whether any contaminants had moved into

the coversoil. In the lime layer, the zone nearest to the underlying tailings was sampled in approximately 0.5 cm increments for a distance of 1.5 cm, and then in 2-4 cm increment to the top of the lime layer. In tailings, the zone nearest to the overlying lime layer was sampled in approximately 0.5 cm increments for a distance of 1.5 cm, and then one additional increment (7.5 cm) was sampled deeper into the tailings unit. Samples were analyzed for pH and contaminants of concern (total As, Cu, Fe, Zn) and the calcium carbonate equivalence in each lime layer was determined (Table 1). 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 standard set forth by the U.S. EPA (ARCO, 2000).

A two-way analysis of variance test was applied to these data sets. In all cases data sets had a normal distribution and 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.

Profile Chemical Characteristics 26 Years After Construction

Separation of coversoil, lime, and tailings layers within the profile were visually very distinct. Based on observation, separation of these layers during sampling was completed with a high degree of certainty. This result allayed concerns that, for example, the lime layer nearest the tailings would be contaminated with tailings as these materials may have been mixed during profile construction. Therefore, interpretation of profile chemistry results is made with the assumption that there was no cross contamination between layers.

Lime Layer Deterioration During A 26-Year Period

These data indicate the lime layer was composed of a by-product of lime manufacturing. When placed over the tailings it had a calcium carbonate equivalence (CCE) of 65.6 ±3.1 % (Table 2). This lime material may have been lime reject as reported by Schafer and Associates (1986) that was mixed with fuel ash during removal from the kiln. The composition of lime reject would have included CaO, $Ca(OH)_2$, $CaCO_3$ and metal contaminants from the ore body and fuel ash. The pH of this industrial by-product would have been >8.5 due to the presence of both CaO and $Ca(OH)_2$. As shown in Table 2, even after 26 years of weathering, note the time of lime reject weathering prior to

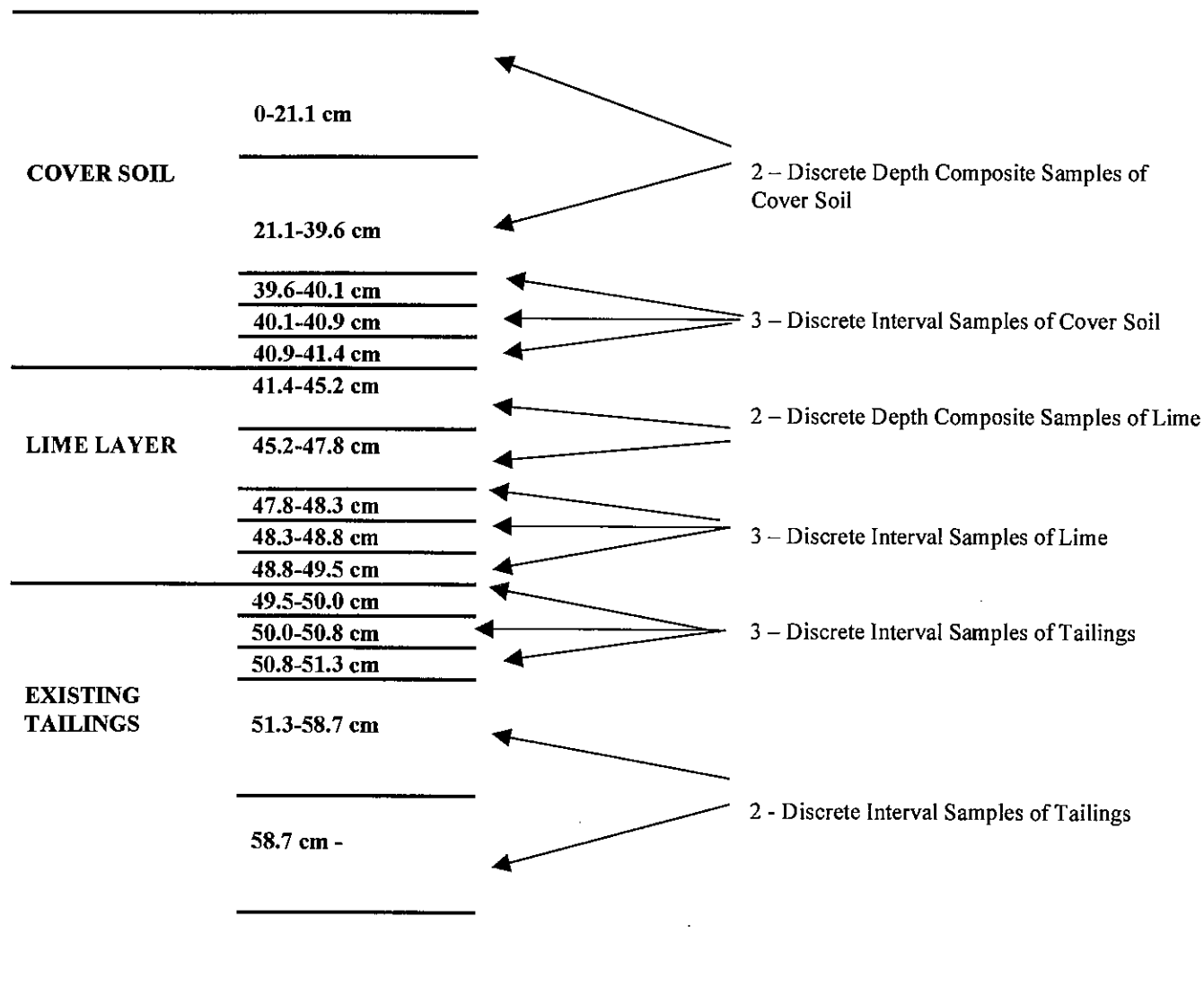Figure 1. Sampling scheme of the coversoil, lime layer and tailings on the Anaconda tailings impoundment.

COVER SOIL

0-21.1 cm

21.1-39.6 cm

2 – Discrete Depth Composite Samples of Cover Soil

39.6-40.1 cm
40.1-40.9 cm
40.9-41.4 cm

3 – Discrete Interval Samples of Cover Soil

41.4-45.2 cm

LIME LAYER

45.2-47.8 cm

2 – Discrete Depth Composite Samples of Lime

47.8-48.3 cm
48.3-48.8 cm
48.8-49.5 cm

3 – Discrete Interval Samples of Lime

49.5-50.0 cm
50.0-50.8 cm
50.8-51.3 cm

3 – Discrete Interval Samples of Tailings

EXISTING TAILINGS

51.3-58.7 cm

2 - Discrete Interval Samples of Tailings

58.7 cm -

Table 1. Analytical methods for soil sample analysis.

Analysis	Method
Total Metals	XRF, Ashe (1995)
Calcium Carbonate Equivalence	Agron. Soc. Amer., Monograph No. 9, Methods of Soil Analysis, 1965, Method 91-4.2, p. 1387.
pH	Agron. Soc. Amer., Monograph No. 9, Methods of Soil Analysis, 1965, Method 62-1.3.2.1, p. 935.

placement on the Anaconda ponds is not known, the pH ranged high as 10.67. This result is somewhat surprising since in-situ treatment of tailings with lime relies on the process that applied CaO and Ca(OH)$_2$ will undergo carbonation within one year and produce a soil profile with a pH <8.5 that is suitable for plant growth. This result demonstrates the need to effectively incorporate a lime product into the soil matrix and not leave clumps of pure lime that may never, meaning decades of time, re-carbonate. The enriched levels of As, Cu and Zn in the lime layer is additional evidence that this is lime reject material and these metal levels are attributable to the presence of fuel ash in this industrial by-product. Metals in fuels, such as coal and coke used to heat the kiln, remain in the ash, which is then disposed of simultaneously with the reject lime.

Analysis of variance indicated the bottom 0.7 cm of the lime layer had a significantly lower CCE, i.e. 23.7 % compared to lime increments sampled more distant from the acidic tailings (Table 2). It is not known whether this loss in neutralizing capacity occurred the first day the profile was constructed or progressively during the entire 26 year age of the profile. The neutralizing capacity of lime materials more distant than 0.7 cm from the tailings were not significantly altered during the 26-year period.

This result impacts future design of the cover placed on this tailings impoundment. A minimum of 46 cm (18 inches) of coversoil must remain suitable for plant growth into the distant future. Assuming the lime had a dry bulk density of 1.47 g/cm^3, meaning 2470 tons per 15.2 cm hectare slice (1000 tons per 6 inch acre slice), then the loss in CCE of 65.6 % to 23.7 % in the 0.7 cm thick lime layer is equivalent to a loss of 43 tons per hectare (17.4 tons per acre) during the 26 year period. It can be hypothesized that if no lime layer had been present, then upward translocation of acidity into coversoil would have occurred for an unknown distance, which may have been a function of the amount of natural CaCO$_3$ present in the coversoil. This result indicates coversoil placed directly over acidic tailings will have a portion of the profile become acidic which then may not be suitable for plant growth. This loss of coversoil suitability would be at least 0.7 cm thick, but the actual thickness is unknown. For this reason, inclusion of a lime layer in this cover design was a requirement (ARCO, 2000).

Required Lime Layer Thickness And Quality

Uncertainty existed whether the upward translocation of acidity into a 0.7 cm thick layer of lime was a constant rate process or a one-time event that occurred the first day of construction. To minimize risk of design failure, it could be assumed this rate of acidification was constant over time (26 years) and will continue at that rate into the future. Of the

three pits sampled in the demonstration area, pit two had the greatest loss of CCE, 57.5 %, in the basal 0.7 cm lime layer, which was equivalent to a consumption of 53.3 tons CaCO$_3$ per hectare.

Consider a design where the lime layer is sufficiently thick to preclude loss of coversoil quality for **200 years**. Given the worst case measured acidification rate of 53.3 tons CaCO$_3$ per hectare per 26 year period, then a lime application of 410 tons CaCO$_3$/hectare/200 years would be required. Assuming a product density of 1.47 g/cm^3, this would be a limestone layer 2.8 cm thick on the tailings impoundment.

However, additional field observations were made at several locations on the tailings impoundment where a 6-9 cm thick layer of lime kiln dust had been applied to the surface of the tailings for a 4-month period of time. The base of this lime layer had a well-defined-thin (2 mm) rust colored coating. Presumably, this coating was an Fe-based precipitate of primarily SO$_4$ and/or CO$_3$. The appearance of the rust zone at the base of the tailings was very similar to that observed in all three pits at the coversoil demonstration. This observation supports a hypothesis that the consumption of lime CCE at the base of the lime layer may be an event that occurs rapidly in time, meaning a few months or less, and then the rate of CCE consumption approaches zero in subsequent months and years.

If it is assumed that there is an initial consumption of lime CCE upon application of the lime layer and no further utilization of the lime CCE in the future, then 53.3 tons CaCO$_3$/hectare may be the maximum amount of reactive lime required as measured in the demonstration area. It was recommended that a minimum of 53.3 tons of reactive CaCO$_3$/hectare be present as a contiguous layer in a constructed lime layer between the tailings and coversoil. Since this is minimum design value, field application would be notably greater to account for construction error.

Based on these data, the chemical content of the lime product applied to the Anaconda tailings impoundment is not an important design consideration. The lime layer measured in this investigation had a relatively low CCE, 65.6 ±3.1 %, and contained notable metal enrichment, which did not contaminate applied coversoil (discussed below). Reject lime materials sampled in test pits varied from an unconsolidated-friable physical state to a consolidated condition comparable to sandstone. Although the lime product used in the future design must contain immediately reactive materials, i.e. a particle diameter <0.25 mm (60 mesh), a portion of the material could contain larger diameter particles.

Table 2. Mean (n = 3) levels of chemical parameters in the coversoil, lime layer and tailings on the Anaconda tailings impoundment.

Average Depth Increment cm	pH	Calcium Carbonate Equivalence %	Arsenic	Iron	Copper	Zinc
				Total mg/kg		
COVERSOIL						
0 - 21.1	7.33 a[1]	-	34 a	23067 a	94 a	80 a
21.1 - 39.6	7.43 a	-	18 b	22267 a	46 a	64 a
39.6 - 40.1	7.40 a	-	17 b	21300 a	47 a	62 a
40.1 - 40.9	7.33 a	-	19 b	21667 a	153 a	71 a
40.9 - 41.4	7.30 a	-	18 b	21733 a	93 a	71 a
LIME LAYER						
41.4 - 45.2	8.67 a	67.9 a	166 a	15500 a	326 a	228 a
45.2 - 47.8	8.97 a	66.6 a	236 a	16300 a	326 a	228 a
47.8 - 48.3	9.68 a[2]	67.0 a[2]	246 a[2]	13396 a[2]	415 a[2]	291 a[2]
48.3 - 48.8	10.37 a	61.0 a	280 a	18333 a	326 a	228 a
48.8 - 49.5	7.67 a	23.7 b	243 a	73600 b	326 a	228 a
TAILINGS ZONE						
49.5 - 50.0	2.27 a	-	146 a	82933 a	245 a	286 a
50.0 - 50.8	2.13 ab	-	116 a	60067 b	162 ab	334 a
50.8 - 51.3	2.23 a	-	97 ab	50400 b	141 ab	331 a
51.3 - 58.7	1.97 b	-	57 b	31067 c	109 b	348 a

[1] Means followed by different letters are significantly different (P = 0.05) for the respective analytical parameter in the specified matrix.
[2] Mean calculated from n = 2.

Translocation Of Metals During A 26-Year Period

These data indicate there was no upward translocation of metals into coversoil during the 26-year period (Table 2). Concentrations of As, Fe, Cu and Zn in coversoil remained at low levels during this period of time. There were no statistically significant differences between metal levels in depth increments sampled through the coversoil, indicating thin layers (0.5 cm) sampled near the base of the coversoil were not accumulating metals. The one exception was where As was present at a significantly more concentrated level (34 mg/kg) in the *surface* of the coversoil, presumably due to deposition of wind blown tailings which were present within 30 m of the test pit area.

As discussed earlier, metal levels in the reject lime layer were enriched, and concentrations of As, Cu and Zn did not vary significantly from the top of the lime layer to the bottom (Table 2). It could be suggested that the enriched metal levels in the lime are due to upward translocation from tailings. If this were the operating mechanism, metal accumulation-precipitation within the lime layer would be at much greater levels at the bottom (near to the tailings) compared to the top of the lime layer. Instead, metal levels are the same throughout the lime layer indicating they are an inherent characteristic emanating from its origin during manufacturing and disposal of the reject lime with fuel ash.

The base layer (0.7 cm thick) of reject lime contained a significantly greater concentration of Fe compared to layers of lime higher in the profile (Table 2). The base of this lime layer had a well-defined-thin (2 mm) rust colored coating. Presumably, this coating was an Fe-based precipitate of primarily SO_4 and/or CO_3 and is the reason for the high Fe content in this layer. During field sampling, the rust coating appeared to be associated with the lime unit lithology as opposed to the tailings, and constituted approximately one-third of the sampled base layer. Due to upward translocation of Fe from tailings, the mean concentration of iron in the base layer (0.7 cm thick) of the lime increased 57,718 mg/kg during the 26-year period. Hypothetically, if this quantity of Fe had translocated into the basal layer of applied coversoil, root growth would not be precluded by the presence of this Fe concentration. Some soils contain an excess in excess of 5% Fe with no apparent toxicity problems (Murphy & Walsh, 1972).

The presence of enriched Fe levels at the base of the lime layer does not impact design of the Anaconda ponds cover. These data indicate upward translocation of Fe from tailings was effectively precipitated for decades of time by as little as a 2 mm thick layer of lime. Construction of a lime layer to treat the upward translocation of acidity from tailings into a lime layer, discussed above, will also successfully precipitate upward Fe translocation.

SEM-EDAX Analysis Of Lime - Tailings Interface

In order to better understand the chemistry associated with the formation rust colored layer located at the tailings/lime layer interface, samples were viewed with the scanning electron microscope (SEM) and the composition determined with energy dispersive analysis of x-rays (EDAX).

In brief, one intact monolith of the lime/tailings interface was collected from the field site and portions of the 1) tailings, 2) rust colored interface zone and 3) lime layer were mounted on stainless steel stubs and all were carbon coated to facilitate SEM observations.

Elemental analysis indicated the lime layer was largely composed of $CaCO_3$ and CaO with 0.8 to 3.5 % Si and lesser amount of other elements. The **tailings** contained notable concentrations of Fe, S, O and 13.8 to 20.2 % Si and lesser amounts of other elements. The rust colored layer contained C, O, S, Fe, Ca (7.2-11.3 %), Si (1.9 to 4.3 %) and lesser amounts of other elements. The Si content of the rust colored zone is representative of the lime and not the tailings. Since Si is immobile in these substrates, this is good evidence that the rust colored zone was part of the base of the lime layer. Therefore, field samplers were correct when they included this rust zone with the basal lime sample. These results support the process that acidity from tailings translocated upward into the lime layer and consumed part of lime CCE. Based on SEM-EDAX analysis, crystals of gypsum ($CaSO_4$) and particles of iron carbonate ($FeCO_3$) were present as a dense layer in the basal lime layer.

Conclusions

Placement of coversoil over a waste material 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 coversoil often do not provide the level of assurance needed to confidently institute impoundment closure projects. Case history observations and measurements of impoundment closures using coversoil become invaluable, as chemical equilibrium has established in the constructed profile over decades of time.

After 26 years, contaminants from acidic-metalliferous tailings failed to migrate up into coversoil when an 8 cm lime layer was present between tailings and coversoil. It was determined a 0.7 cm thick lime layer would have

prevented upward migration of contaminants during the 26 year period. Therefore, in the future a 0.7 cm lime layer will be constructed between coversoil and tailings in this project area.

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