Salinity/pH Interactions and Rooting Morphology in Monolayer Soil Covers above Copper Tailings

M.A. Milczarek *GeoSystems Analysis, Inc., USA*

F.M. Steward, Jr *Freeport McMoRan Copper & Gold Inc., USA*

W.B. Word *Freeport McMoRan Copper &Gold Inc., USA*

M.J. Buchanan *GeoSystems Analysis, Inc., USA*

J.M. Keller *GeoSystems Analysis, Inc., USA*

Abstract

In an effort to understand rooting morphology and the long-term potential for upward migration of solutes from tailings of varying geochemical conditions into evapotranspirative cover systems, test trench investigations were conducted in cover systems of varying thicknesses and ages of up to 19 years in the southwestern USA. Test trench surveys consisted of measuring: cover system thickness; tailings/cover material mixing at the contact, and; root characteristics (i.e. size, abundance and maximum rooting depth). Soil samples were collected at various depths below ground surface and at the tailings/cover system contact and tailings samples were collected below the contact. Rooting surveys and soil sample collections were replicated in at least 3 locations per test trench. All soil and tailings samples were laboratory tested for 1:1 soil:water extract electrical conductivity (EC) and pH. Selected composite samples were tested for a spectrum of plant nutrients and acid neutralization potential.

Data from these studies indicates that rooting density is generally common throughout the shallow cover systems and does not exhibit strong exponential decay. Significantly different increased salinity or decreased pH conditions in the cover system were limited to within 15 cm of the cover system directly above the cover/tailings contact. High variability in geochemical results was observed with the extent of upward migration and accumulation of solutes in the cover soils generally depending on the tailings and cover system geochemical conditions and the cover system thickness. Increased tailings acidity and pyrite content generally resulted in decreased pH and increased EC above the tailings/cover contact. Cover material neutralization capacity may also likely play a role in controlling potential salinization/acidification.

1 Introduction

In the semi-arid and arid Southwestern USA, shallow monolayer evapotranspirative (ET) covers (i.e. < 90 cm) have been shown to be effective in limiting downward infiltration and net percolation of precipitation into closed landfills and mine waste facilities (i.e. Dwyer, 2003, Albright et al., 2004, Milczarek et al., 2009). In the case of copper mine tailings, low pH and high electrical conductivity (EC) raise concerns regarding the potential loss of ET cover system function (the ability to support vegetation) due to upward migration of salinity and acidity into the cover materials. Salinization has not been observed in shallow cover soils over circumneutral tailings (Milczarek et al, 2006), whereas other authors have reported limited upward salinity migration from acidic tailings into reclaimed mine-spoil cover soils on time-scales up to 25 years (i.e. Dollhopf et al., 2001, Dollhopf et al., 2003, Munk et al., 2000). Munk et al. (2006) also observed decreased pH, increased EC and decreased acid neutralization potential (ANP) at depths of 5 to 10 cm in shallow cover material (40 cm to 60 cm thick) above acidic tailings.

The mechanisms for upward salinity and acid migration include advection and diffusion. Diffusion processes are controlled by the concentration gradient of protons and soluble salts across the interface between the tailings and cover system (tailings/cover contact) and can generally be considered time-dependent. That is, if diffusion is the dominant process, salinization of a cover system from underlying tailings will progressively increase over time. Advection of water that has come into contact with the underlying tailings and subsequently into a cover system is dependent on hydraulic gradients and the unsaturated hydraulic conductivities of both the tailings and cover system material under existing soil water pressure potential conditions. In general, upward hydraulic gradients exist when the upper soil profile is much drier than the underlying tailings. Under these conditions, the unsaturated hydraulic conductivities are typically very low (i.e. < 10^{-9} cm/sec) and net advection should be similarly low (i.e. < 0.05 cm/yr). If the ET cover system is adequately storing and releasing precipitation, then the tailings should remain dry and upward salinity migration from advection should be minimal. An exception to these conditions could occur under episodic wet periods whereby the underlying tailings become sufficiently wet to increase the unsaturated hydraulic conductivities to allow measurable upward flux resulting from upward hydraulic gradients during the subsequent drying period. Nonetheless, advection rates will be controlled by the soil water characteristic curve (SWCC) of the cover soil, such that finer-grained cover soils would be expected to have higher upward advection rates than coarse-grained cover soils as a result of greater hydraulic conductivities under medium to low pressure potential conditions.

There is minimal literature on salt tolerance and the effect of elevated metal and/or metalloid concentrations on native species. Some native species (i.e. phreatophytes) are known to have low tolerance for salinity whereas other upland, halophyte shrubs may be highly tolerant. In general, native reclamation species commonly used in the western USA show moderate to high tolerance for salinity and elevated metal concentrations (Barth 1986, Schafer, 1979, Pascke and Redente, 2002). If an ET cover system were to become partially salinized (i.e. just above the tailings/cover contact), the effect on native vegetation is likely to be minor, and simply result in a shift to more salt tolerant species. Nonetheless, due to evolutionary considerations, vegetation native to the semi-arid and arid southwestern USA are commonly found in neutral to alkaline pH soil conditions.

Rooting characteristics in ET covers are poorly understood. Using the predictive model proposed by Schenk and Jackson (2002) for root distribution in semi-desert shrublands in the southwestern USA, rooting should exhibit an exponential decline with depth below surface. For examples, in a 60 cm cover system, the uppermost 10 cm of the cover profile should have a rooting density 4 to 5 times greater than the lowest 10 cm. However, rooting in shallow ET covers over acid tailings seem to be common throughout the entire depth of the shallow cover system, and in the case of circumneutral tailings, can significantly penetrate into the tailings (Milczarek et al., 2006). Relatively uniform root distribution over a short depth interval (i.e. < 60 cm) may occur if roots that would normally extend to depth propagate throughout the shallow cover material.

In an effort to understand rooting morphology and the long-term potential for upward migration of solutes from tailings of varying geochemical conditions into ET cover systems, five test trench investigations were conducted in four different cover systems of varying thicknesses and age in the Southwestern USA. Cover system ages ranged from five years to 19 years; two of the investigations were in the same cover material at 5 and 10 years after placement. Data was collected to assess rooting density and distribution, soil pH and EC, and a variety of nutrients and plant-available metals to determine whether upward migration of salts, proton acidity, and metal transport had occurred at each of these locations.

2 Site Background

Four different cover systems located at two different mine sites in southwestern Arizona, USA were investigated between 2002 and 2007 (Table 1). The Copper Tailing Storage Area (CTSA) Side-slope and Demonstration cover systems located near Bisbee, Arizona, were investigated in 2007 and are on tailings side-slope areas reclaimed separately in 1988 and 2000. The Tailings 4W and SW2 cover systems are near Morenci, Arizona. The Tailings 4W area is a series of reclamation test plots on tailings side-slopes that were investigated at 5 and 10 years after placement in 1997. The Tailings SW2 area consists of tailings dam benches that were investigated in 2004, 10 years after reclamation in 1994.

Bisbee is in the Madrean archipelago with vegetation representative of upland Sonoran Desert scrub. Morenci is located at the edge of the Madrean Archipelago between the northwestern Chihuahuan Desert and the northeastern Sonoran Desert. Vegetation in the area is a mix of shrubs/forbs and grasses representing both Sonoran Desert scrub and Chihuahuan Desert species.

The CTSA areas are at an approximate elevation of 1460 m above mean sea level (amsl) and receive on average 452 mm of precipitation per year. The Tailings 4W and SW2 areas are located at approximately 1220 m and 1120 m amsl, respectively, and the Morenci area receives an average of 337 mm of precipitation per year. Both locations are under bi-modal precipitation regimes with 55% to 60% of precipitation occurring from intense summer monsoon storms and the remainder as winter frontal system rain and snow.

Normal monthly average temperatures in Bisbee range from approximately 7.4 and 24.5 degrees C in January and July, respectively. Mean monthly temperatures in Morenci range from 7.9 and 29.9 degrees C in January and July, respectively. Morenci is considerably warmer during the summer months: the average monthly maximum temperatures exceed 34^{o}C from June through September, whereas the average maximum monthly temperatures observed in Bisbee are 32.1 degrees C in June. At both sites freezes are possible from November through March. The estimated reference evapotranspiration (ETo) for both sites exceed 1700 mm per year, from about 64 mm in January to over 250 mm in June.

Cover system borrow material at the CTSA site is the Glance Conglomerate, a mid-Mesozoic basal unit of the Lower Cretacaous Bisbee group. The Glance Conglomerate is typically dominated by 50% to 70% gravels and cobbles (> 2 mm), with the remaining fine-earth fraction classified as a loam or clay loam. Placement of the Glance Conglomerate was primarily for dust control and rock armor, consequently, vegetation establishment is generally minor and variable within the cover areas. The borrow material for Tailings 4W and SW2 is from the Gila Group, a Pleistocene-Miocene aged conglomerate rich unit that is classified as a gravelly or cobbly sandy loam. Both materials are skeletal, though the Glance Conglomerate is both coarser in the > 2 mm fraction, and finer-grained in the < 2mm fraction, than the Gila Conglomerate.

The physical properties of the CTSA, SW2 and 4W tailings are similar and characteristic of tailings dam material, ranging from loamy sand to clay loam. The pyrite concentrations however are significantly different: material from Tailings SW2 averages less than 2% pyrite, Tailings 4W samples averaged approximately 5% pyrite, and the CTSA tailings pyrite contents range from 6% to 12%.

Table 1. Monolayer cover systems over copper tailings investigated

Monolayer Cover System Location	Age of Cover System (years)	Cover Depth Mean (cm)	Number of Test Trenches	Cover Material Type	Geochemical Sample Interval[1]	Rooting Survey Sample Depths[1]
CTSA South Slope (2007)	19	33 to 97 cm Mean = 64 cm	6	Very gravelly to Extremely cobbly loam to clay loam	2.5 - 10 cm bgs 17.5 - 25 cm ac 10 - 17.5 cm ac 2.5 - 10 cm ac 2.5 – 10 cm bc	NA[2]
CTSA Demonstration (2007)	7	54 to 80 cm Mean = 68 cm	4	Very gravelly to Extremely cobbly loam to clay loam	2.5 - 10 cm bgs 17.5 - 25 cm ac 10 - 17.5 cm ac 2.5 - 10 cm ac 2.5 – 10 cm bc	N A[2]
Tailings 4W 30 cm & 60 cm Covers (2002)	5	26 to 53 cm Mean = 41 cm	16	Gravelly to Very gravelly sandy loam	2.5 - 7.5 cm bgs 10 - 15 cm ac 5.0 - 10 cm ac 0 - 5.0 cm ac 2.5 - 7.5 cm bc	0 - 10 cm bgs 10 - 20 cm bgs 0 - 10 cm ac
		44 to 82 cm Mean = 61 cm	16			
Tailings 4W 30 cm & 60 cm Covers (2007)	10	35 to 46 cm Mean = 42 cm	12	Gravelly to Very gravelly sandy loam	2.5 - 7.5 cm bgs 17.5 - 22.5 cm ac 12.5 - 17.5 cm ac 7.5 - 12.5 cm ac 2.5 - 7.5 cm ac 2.5 - 7.5 cm bc	0 - 10 cm bgs 10 - 20 cm bgs 0 - 10 cm ac
		62 to 85 cm Mean = 70 cm	12			
Tailings SW2 (2004)	10	51 to 84 cm Mean = 68 cm	9	Gravelly to Extremely cobbly sandy loam	2.5 - 7.5 cm bgs 10 - 15 cm ac 5.0 - 10 cm ac 0 - 5.0 cm ac 2.5 - 7.5 cm bc	0 - 10 cm bgs 10 - 20 cm bgs 0 - 10 cm ac

[1] bgs = below ground surface; ac = above tailings/cover contact; bc = below tailings/cover contact (tailings)
[2] Rooting surveys not performed

3 Methods

Due to differences in study objectives, the scope of investigation varied between sites. The Tailings 4W area contained test plots with different cover thicknesses (30 cm and 60 cm) and treatments/amendments (biosolid/no biosolids), consequently, the total number of test trenches in Tailings 4W was greater than for the other sites (Table 1). The 2002 Tailings 4W and 2004 Tailings SW2 studies focused primarily on sampling and testing cover soil pH and EC values at different depths in the cover profile and only tested selected samples for soil fertility and acid neutralization potential (ANP, % $CaCO_3$). In addition to testing for cover soil pH and EC at specific depth intervals, the 2007 Tailings 4W study also tested soil fertility and ANP testing on composited depth interval samples, whereas the CTSA studies only tested for soil fertility and ANP on selected samples (no composites).

Test trenches were backhoe-excavated through the cover material to a depth of approximately 30 cm below the tailings/cover system contact at the frequency shown in Table 1; trenches were typically between 3 to 4 meters long and one meter wide. Test trench surveys consisted of measuring the following in three replicate profiles per trench: cover system thickness: thickness of tailings/cover material mixing at the contact and root size and density, Soil and tailings samples were collected for geochemical testing using hand trowels in 5 cm increments above (ac) and below (bc) the tailings/cover system contact at the depths shown in Table 1 for the Tailings 4W and Tailings SW2 sites; the coarse nature of the CTSA cover material required a 7.5 cm sample interval. Initial surveys conducted in 2002 (Tailings 4W) and 2004 (Tailings SW2) collected samples at 0 to 5 cm, subsequent surveys conducted in 2007 collected samples at 2.5 cm to 7.5 cm ac to minimize the potential for sample bias from mixing of the tailings and cover system.

All soil and tailings samples were air dried and sieved through a #10 mesh (- 2 mm) and laboratory tested for 1:1 soil:water extract electrical conductivity (EC) and pH. For the 2007 Tailings 4W investigations, samples from replicate depth intervals in each test plot (two trenches) were composited for soil fertility and ANP testing (i.e. six replicate samples at the 2.5 cm to 7.5 cm below ground surface (bgs), and at 12.5 to 18 cm and 2.5 to 7.5 cm above the contact (ac) were composited). For the CTSA investigations, composite samples were created from three different depth intervals (2.5 to 10 cm ac, 10 to 17.5 cm ac and 2.5 to 10 cm bgs) to characterize two South Slope trenches that showed low pH and neutral pH cover material. One Demonstration plot trench was also composited at similar depth intervals. Soil fertility parameters included plant-available concentrations of: calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), nitrate-nitrogen (NO3), phosphate-phosphorus (PO4), sulfate-sulfur (SO4), zinc (Zn), iron (Fe), manganese (Mn), copper (Cu), boron (B), exchangeable sodium percentage (ESP), and 1:1 soil-water paste pH and EC. In addition, composite samples were also tested for ANP. Only Cu, Fe, SO_4 and ANP will be discussed herein because of their relevance to copper tailings, pyrite oxidation and acid neutralization processes.

At the Tailings SW2 and 4W areas, root size and root density distribution, cover and contact characteristics, and water content were described at the three profile locations in each trench using NRCS classification (Schoeneberger et al., 2002), modified for desert scrubland conditions. Rooting surveys were not conducted at the CTSA areas. For each profile, root descriptions were made for three 10-cm by 10-cm areas at the depths shown in Table 1. Estimated root fiber diameters were classified as: Very Fine (0 to 1 mm); Fine (1 to 2 mm); Medium (2 to 5 mm); Coarse (5 to 10 mm). Root abundance was classified in terms of number of root fibers per 10-cm by 10-cm square as: Few (< 10 for very fine or fine; <1 for medium or coarse; Few-Common – 10-25 for fine or very fine; 1-2 for medium; 1 for coarse; Common – 25-100 for fine or very fine; 2-10 for medium; 2-5 for coarse, and; Many – > 100 for fine or very fine; ≥ 10 for medium; ≥5 for coarse. The distance above the contact at which rooting was first evident and abundant root concentrations or root-matting when present, were also recorded.

4 Results

Cover material thickness varied across the sites with the least variance observed in the 4W 30 cm cover trenches and the greatest variation in the CTSA South Slope test trenches (Table 1). In almost all cases, the transition between the tailings/cover contact was distinct, mixing of tailings and cover material was not typically observed. In some trench profiles, visible precipitate staining was observed immediately above the tailings/cover contact; however, this phenomenon was not observed in Tailings SW2 trenches and was infrequently observed in Tailings 4W. Visible precipitate staining occurred from 0 to 8 cm ac in the CTSA

Demonstration cover material, and up to depths of 20 cm ac in the CTSA South Slope Cover material (Figure 1). The degree and depth of staining was highly variable within individual trenches. Microscopic analyses were conducted to classify the precipitate and assess whether the staining was from tailings mixed with the cover material. These analyses indicated staining was due to iron precipitates (e.g. jarosite) coating Glance Conglomerate cover material, suggesting acid neutralization and precipitation reactions had occurred since placement of the cover material.

Figure 1. Typical tailings/cover contact in the Tailings 4W trenches on left, precipitate staining on above the tailings/cover system contact in the CTSA South Slope (right) area

4.1 Tailings 4W and SW2 Geochemical Data

4.1.1 1:1 Extract pH and EC

Mean pH and EC values by test trench area and sampling depths are shown in Table 2 for the Tailings 4W and SW2 areas. Tailings 4W samples in 2002 and 2007 showed decreasing mean pH values in the neutral range (6 to 8) decreasing with depth from 5 cm bgs to 10 cm ac in both cover depths; mean pH values in the first sample collected above the tailings/cover contact (5 cm ac in 2007, 2.5 cm ac in 2002), were moderately acidic (between 4.0 and 5.8) for both cover depths. The mean pH values for all tailings samples (5 cm bc) were less than 3. In both 2002 and 2007, mean EC values in the cover increased with proximity to the tailings/cover contact (Table 2). The mean cover EC values were relatively low (under 1.5 dS/m) for sample intervals above 10 cm ac, but ranged between 1.6 and 3.9 dS/m in samples closer to the tailings/cover contact.

Variance in pH and EC values increased with proximity to the tailings/cover contact with the highest standard deviations occurring at the first or second sample above the contact (Table 2). In both the 2002 and 2007 sampling events, pH was observed to range by as much as two standard units between individual profiles within a single trench, at the proximal tailings/cover contact depths (e.g. pH values from 4 to 6 at 5 cm ac). The correlation between EC and pH was high in the 2002 sampling event (R^2 = 0.86, 30 cm cover; R^2 = 0.83, 60 cm cover), but R^2 values decreased to less than 0.72 in the 2007 event, primarily due to decreased EC values observed in samples proximal to the tailings/cover contact and also in samples from the tailings. Similarly, the slightly increased pH observed in 2007 compared to 2002, indicates that ongoing neutralization may be occurring.

ANOVA comparisons of mean pH, EC and selected soil fertility parameters are also presented in Table 2: different alphabetical symbols indicate significant differences between the cover depth sample intervals within a treatment; bolded alphabetical symbols indicated significant differences between treatments at the same sample depth interval.

Table 2. 1:1 Extract pH, EC and selected fertility parameters vs depth for Tailings 4W and SW2 investigations

Cover Type	Avg Depth Relative to Contact (cm)	1:1 Paste pH			1:1 Paste EC			DTPA-Extractable Fe[1]			DTPA-Extractable Cu[1]			Hot Water-Extractable SO_4[1]			Acid Neutralization Potential		
		SU	*std dev*	Sig[2]	(dS/m)	*std dev*	Sig[2]	ppm	*std dev*	Sig[2]	Ppm	*std dev*	Sig[2]	ppm	*std dev*	Sig[2]	% $CaCO_3$	*std dev*	Sig[2]
4W 30 cm Cover (2007)	36	7.0	*0.6*	A	0.57	*0.51*	A	15	*11*	A	43	*26*	A	89	*61*	A	2.84	*1.41*	AB
	20	6.9	*0.9*	**A**	0.89	*0.86*	**AB**	--	--	--	--	--	--	--	--	--	3.35	*0.71*	A
	15	6.8	*1.0*	**A**	1.09	*0.99*	AB	--	--	--	--	--	--	--	--	--	3.30	*0.81*	A
	10	6.3	*1.2*	**A**	1.52	*1.06*	B	19	*31*	A	9	*8*	B	353	*600*	AB	3.03	*1.29*	AB
	5	5.2	*1.1*	**B**	2.32	*0.81*	C	48	*34*	A	12	*8*	AB	886	*378*	B	2.01	*0.73*	B
	-5	2.9	*0.2*	C	3.08	*0.82*	D	--	--	--	--	--	--	--	--	--	--	--	--
4W 30 cm Cover (2002)	37	7.0	*0.1*	A	0.48	*0.16*	A	--	--	--	--	--	--	--	--	--	--	--	--
	12.7	6.4	*0.9*	A	1.24	*1.30*	A	--	--	--	--	--	--	--	--	--	--	--	--
	7.6	5.3	*1.3*	**B**	2.82	*1.48*	**B**	--	--	--	--	--	--	--	--	--	--	--	--
	2.5	4.0	*0.7*	C	3.90	*1.27*	BC	--	--	--	--	--	--	--	--	--	--	--	--
	-5	2.6	*0.2*	D	5.59	*1.67*	C	--	--	--	--	--	--	--	--	--	--	--	--
4W 60 cm Cover (2007)	56	7.1	*0.3*	B	0.41	*0.23*	A	8	*5*	A	32	*20*	A	33	*21*	A	3.63	*0.91*	A
	20	7.4	*0.3*	**A**	0.51	*0.55*	**A**	--	--	--	--	--	--	--	--	--	4.07	*2.40*	A
	15	7.2	*0.4*	**AB**	0.76	*0.75*	AB	--	--	--	--	--	--	--	--	--	4.03	*2.35*	A
	10	6.9	*0.9*	**B**	1.12	*0.96*	B	4	*0*	A	5	*6*	A	111	*128*	A	3.67	*2.17*	A
	5	5.8	*1.3*	**C**	2.16	*0.97*	C	37	*27*	A	15	*21*	A	648	*230*	B	3.10	*2.23*	A
	-5	2.9	*0.2*	D	3.17	*0.61*	D	--	--	--	--	--	--	--	--	--	--	--	--
4W 60 cm Cover (2002)	65	7.0	*0.3*	A	0.72	*0.83*	AB	--	--	--	--	--	--	--	--	--	--	--	--
	12.7	6.9	*0.2*	A	0.71	*0.56*	A	--	--	--	--	--	--	--	--	--	--	--	--
	7.6	6.0	*0.2*	**B**	1.64	*1.06*	**B**	--	--	--	--	--	--	--	--	--	--	--	--
	2.5	4.3	*0.2*	C	3.17	*0.76*	C	--	--	--	--	--	--	--	--	--	--	--	--
	-5	2.5	*0.3*	D	5.58	*0.73*	D	--	--	--	--	--	--	--	--	--	--	--	--
SW2 60 cm Cover (2004)	58	7.8	0.20	A	0.72	1.01	AB	--	--	--	--	--	--	--	--	--	14.3[3]	*2.09*	--
	12.5	7.7	0.20	A	0.88	0.91	A	--	--	--	--	--	--	--	--	--	--	--	--
	7.5	7.8	0.21	A	0.92	0.84	A	--	--	--	--	--	--	--	--	--	--	--	--
	2.5	7.6	0.18	A	1.69	1.04	B	--	--	--	--	--	--	--	--	--	15.5[3]	*2.23*	--
	-10.5	3.1	0.61	B	2.58	1.76	AB	--	--	--	--	--	--	--	--	--	--	--	--

[1] Composite samples from six samples at each specified depth interval; -- signifies samples were either not composited or tested at these intervals

[2] Different letters indicate a significant difference (p=0.05) between mean values at depth intervals within cover depth treatment; bold letters indicate significant mean difference at depth intervals between cover depth treatment

[3] ANP values for Tailings SW2 were averaged from different (non-composite) samples at the specified depth intervals

ANOVA comparisons of mean pH values by sample depth interval, within cover depth treatment, shows significantly different mean pH values ($p=0.05$) for the tailings and the first one (2007) or two (2002) sample depths above the tailings/cover contact compared to the upper cover depths (Table 2). Similar trends were observed for mean EC at different depths, with the exception of the 2007, 30-cm cover sampling event which showed intermediate EC at 20 cm ac.

ANOVA comparisons of cover depth effects show pH was significantly higher in the 60 cm cover than the 30 cm cover at sample depths from 5 cm to 20 cm ac in the 2007 event (Table 2), whereas, treatment differences were only significant at the 7.6 cm ac interval in the 2002 event. The observed significant difference in mean pH between the 60-cm and 30-cm cover depths in 2007 results from approximately twice as many profile samples with low pH values in the 30 cm cover than in the 60 cm cover. Although lower mean EC values were observed in the 60 cm cover compared to the 30 cm cover at similar depths (Table 2), significant differences in EC were only observed at 20 cm ac in 2007 and at 7.6 cm in 2002. Due to differences in sample depths, ANOVAs could not be run to compare the 2002 and 2007 sample events.

The Tailings SW2 area showed higher mean pH values in the cover system and tailings across all depth intervals compared to the Tailings 4W area data (Table 2); different capping sources were used for the Tailings 4W and SW2 reclamation. Significant differences in mean pH values were not observed in any of the Tailings SW2 cover depth intervals. However, similar to the Tailings 4W cover, Tailings SW2 showed slightly increasing mean EC values with proximity to the tailings/cover contact. A significant difference in mean EC occurred at the 2.5 cm ac depth interval compared to samples farther above the contact.

4.1.2 Iron, Copper, Sulfate and Acid Neutralization Potential Data

The results of extractable Fe, Cu, SO_4 and ANP in composite samples from the two cover depths at Tailings 4W are shown in Table 2. Although elevated levels of extractable Fe were observed at the 5 cm ac depth, sample variance was high and these values were not significant at $p=0.05$. Extractable Cu showed the highest mean values at the surface (5 cm bgs) in both cover depth treatments with only slightly elevated Cu at 5 cm ac; significant were only observed at 10 cm ac in the 30 cm cover depth treatment.

Extractable SO_4 levels were elevated at both 5 cm ac and 10 cm ac, however, variance was high and significant differences were only observed at the 5 cm ac interval in the 30 cm and 60 cm cover depth treatments (Table 2). Of note, mean SO_4 for samples at 15 cm ac in the 30 cm depth treatment were not significantly lower than the mean for 5 cm ac. Mean ANP values were moderate ($CaCO_3$=2% to 4%) and generally decreased with proximity to the tailings/cover contact in both cover depth treatments (Table 2). However, a significant difference was only observed at the 5 cm ac depth interval in the 30 cm cover depth treatment. Mean ANP values also decreased in the 5 cm bgs surface samples, possibly due to effects from the biosolids addition. Of note, only three out of 64 composites samples showed ANP values less than 1% as $CaCO_3$, indicating residual neutralization capacity even in cover samples with pH less than 6.

Four samples collected for ANP testing at the Tailings SW2 cover system at the 2.5 cm ac and 2.5 cm bgs depth intervals indicated very high ANP values (> 14%) with no decrease in ANP with depth.

4.2 CTSA Demonstration and South Slope Area Geochemical Data

Mean pH and EC values by test trench area and sampling depths are shown in Table 3. The CTSA Demonstration plots showed alkaline pH (> 7) conditions from the tailings/cover contact to 6.3 cm bgs with no significant differences observed in mean pH between depth intervals. Mean EC values were moderate (1.7 to 2.5 dS/m) within the Demonstration cover material, and generally increased with depth from ground surface to above the tailings/cover contact. A significant increase in mean EC was observed at 6.3 cm ac with intermediate EC values at 13.8 cm ac and 21 cm ac.

The CTSA South Slope area depth intervals showed decreasing mean pH values from the surface (6.3) to above the tailing/cover contact (5.7). Mean EC values were moderately saline (2.3 to 3.9 dS/m) with increasing EC in proximity to the tailing/cover contact.

Table 3. 1:1 Extract pH, EC and selected fertility parameters vs depth for CTSA investigations

Cover Type	Avg Depth Relative to Contact (cm)	1:1 Paste pH SU	1:1 Paste pH *std dev*	1:1 Paste pH Sig[1]	1:1 Paste EC (dS/m)	1:1 Paste EC *std dev*	1:1 Paste EC Sig[1]
CTSA Demonstration Plots 60 cm Cover (2007)	58.5	7.2	*0.3*	A	1.65	*0.70*	A
	21.3	7.3	*0.2*	A	2.02	*0.44*	AB
	13.8	7.2	*0.2*	A	2.12	*0.39*	AB
	6.3	7.1	*0.2*	A	2.50	*0.34*	B
	-6.3	2.3	*0.4*	B	12.5	*3.44*	C
CTSA South Slope 60 cm Cover (2007)	57.9	7.0	*0.4*	A	2.27	*0.92*	A
	21.3	6.8	*1.1*	A	2.67	*1.53*	A
	13.8	6.2	*1.4*	AB	3.35	*2.51*	A
	6.3	5.7	*1.6*	B	3.92	*3.45*	AB
	-6.3	3.2	*1.3*	B	7.34	*3.91*	B

CTSA Trench Composites	Avg. Depth relative to contact (cm)	DTPA Extractable[2] (ppm) Fe	DTPA Extractable[2] (ppm) Cu	Hot Water Extractable SO_4[2] (ppm)	Acid Neutral-ization Potential[2] (% $CaCO_3$)
South Slope (SS9)	47.0	20	130	830	5.70
	13.8	32	160	1000	2.90
	6.3	28	190	920	3.10
South Slope (SS11)	87.7	3	29	650	4.30
	13.8	31	72	1200	0.20
	6.3	130	70	2700	0.00
Demonstration Plot (DP4)	69.9	7	72	560	13.70
	13.8	6	65	570	13.50
	6.3	13	79	1000	11.80

[1] Different letters indicate a significant mean treatment difference at p=0.05
[2] Composite samples from three samples at each specified depth interval

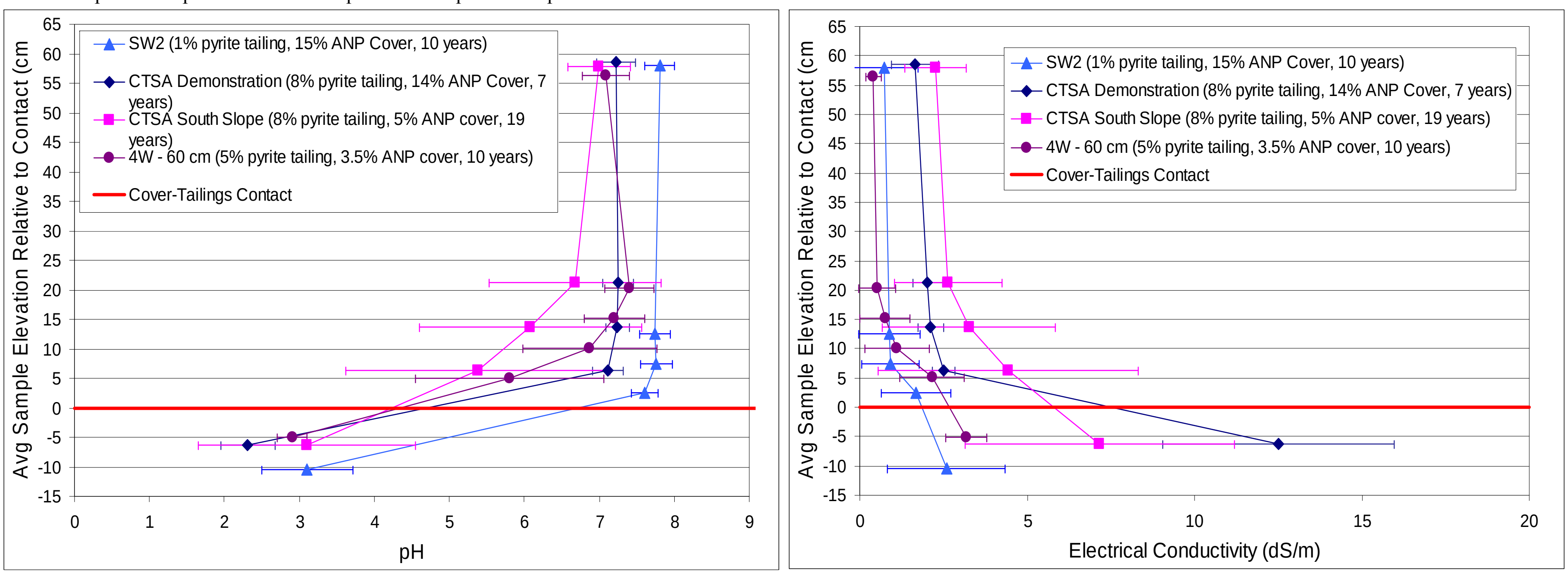

Figure 2. 1:1 Extract pH and EC vs depth interval in relation to tailings/cover contact for Tailings SW2, 4W, CTSA Demonstration and South Slope Areas

Variability in CTSA South Slope measurements was higher than in the Tailings 4W study, primarily due to two (of 6) trenches where pH was observed to range by as much as three SU between individual profiles within a trench. The CTSA South Slope area showed generally lower pH and higher EC values than the Demonstration plot areas, however, significant differences in mean pH were only observed at the 6.3 cm ac depth interval with an intermediate value at 13.8 cm ac.

Table 3 also presents extractable Fe, Cu, SO_4 and ANP results for depth interval composites selected to represent a circumneutral cover (SS9) and a pH/EC affected cover (SS11) from the CTSA South Slope trenches, in addition to composites from the Demonstration plot trenches (DP4). In circumneutral cover sample SS9, there were no trends observed in the Fe, Cu or SO_4 data, whereas ANP values appeared to be slightly lower in the 6.3 cm and 13.8 cm ac depths than at 47 cm ac. The SS11 sample showed elevated Fe, Cu and SO_4 values and low ANP at the 6.3 cm and 13.8 cm ac sample depths. DP4 showed slightly elevated SO_4 and decreased ANP at the 6.3 cm ac sample depth.

4.3 Evaluation of Tailings 4W, SW2 and CTSA Demonstration and South Slope Area Geochemical Data

Similar trends of decreasing mean pH and increasing mean EC values in proximity to the tailings/cover contact were observed at each of the Tailings 4W, SW2 and the CTSA Demonstration and South Slope areas. However, the magnitude of change and variance in the data differed between sites. Figure 2 shows the mean pH and EC values and standard deviation at various depth intervals in the average 60 cm covers. The cover system least affected by decreased pH and increased EC above the tailings/cover contact was Tailings SW2, which can be characterized as a low acid generating potential (AGP) tailings (pyrite <1%) with a high ANP cover (15% $CaCO_3$). The CTSA Demonstration had high ANP cover (14% $CaCO_3$) and did not show pH effects, even though it overlies high AGP tailings (8% pyrite).

Both the Tailings 4W and CTSA South Slope cover material showed greater changes in mean pH and EC at the various depth intervals, in addition to having much higher data variance than the Tailings SW2 and CTSA Demonstration areas (Figure 2). Both these areas are characterized by moderate to high AGP tailings with moderate to low ANP cover materials. A comparison of the sample data sets indicates that the Tailings 4W and CTSA South Slope 60 cm cover samples showed pH < 5 in only 20% and 25%, respectively of the samples between 5 cm and 15 cm ac, respectively. Less than 4% and 6% of the samples, respectively at higher elevations above the tailings/cover contact at these areas showed pH <5. The Tailings SW2 and CTSA Demonstration areas had no cover samples at any depth with pH < 5. Consequently, the greater mean pH and EC effects shown in these covers (Figure 2) are spatially variable.

Between the 2002 and 2007 Tailings 4W sampling events there appeared to be slight decreases in EC and increases in pH in the tailings samples and cover samples from 5 to 15 cm above the tailings/cover contact. Higher mean tailings pH was also observed below the 19 year-old CTSA South Slope than the 7-year old CTSA Demonstration cover. These data indicate that significant pH and salinity effects on the cover system were limited to a fraction of the cover system volume and that progressive degradation over time may be limited by rinsing of the cover system from deep percolation. As previously noted there is residual cover material ANP even in areas of decreased pH, suggesting ongoing neutralization reactions may continue to mitigate pH effects.

Differences in EC, pH and ANP values between the Tailings 4W cover depth treatments indicate acidity and salinity effects were greater in the 30 cm cover than in the 60 cm cover at equivalent depths above the contact. Because the cover depth sample intervals in the 30 cm cover are approximately 30 cm closer to the surface than the 60 cm cover depth sample intervals, hydraulic gradients which drive upward advective flux should be higher at the tailings/cover contact in the 30 cm cover than the 60 cm cover depth.

The absence of significant change in high ANP covers, observed greater effects in 30 cm cover depths than in 60 cm cover depths, observed iron precipitation and spatial variability in cover geochemical conditions indicate the migration of tailings solution via advection; diffusion may also be a secondary cause of decreased pH and increased EC at cover depths proximal to the tailings/cover contact. If diffusion were the primary cause, EC and pH levels would be expected to be generally uniform across cover depth intervals. The observed spatial variability in geochemical conditions is consistent with spatial variability in cover hydraulic properties and variable infiltration of precipitation (i.e. preferential flow) into the cover system.

Nonetheless, tailings wetting and subsequent evapotranspirative drying will result in advection only if sufficient infiltration occurs to increase soil water pressure potentials at the tailings/cover contact such that the cover material hydraulic conductivity is sufficiently high to allow upward advection (i.e. $K > 10^{-6}$ cm/sec). Subsurface monitoring of the Tailings 4W cover systems between 2000 and 2009 indicates that significant tailings wetting only occurred during abnormally high precipitation conditions in October 2000 and February 2005 (Milczarek, et al. 2009). Moreover, subsequent evapotranspirative demand needs to be sufficiently high to rapidly dry the cover profile and create upward hydraulic gradients from the tailings. These requirements indicate that high precipitation/deep wetting periods in the summer are more likely to cause advection of tailings solution than winter events. Extrapolation of the precipitation intensity-subsurface response data indicates three summertime deep wetting periods may have occurred at both Morenci and Bisbee between 1988 and 2000 and none between 2001 and 2007. It should also be noted that upward flux conditions are short-term and most likely limited to a small distance above the tailings/cover contact due to rapid decreases in hydraulic conductivity as the cover dries. Consequently, advection of tailings solution into the cover system is likely to be episodic and may be limited to a very shallow region above the tailings cover contact.

The effects on vegetation from lower pH and higher EC conditions at cover depths proximal to the tailings/cover contact are generally believed to be minor. Volume calculations based on individual pH values at specific depths in the Tailings 4W covers indicate that less than 3% and 10% of the 60 cm and 30 cm cover volume showed pH < 5 respectively. Similar affected volumes (<6%) are calculated for the CTSA South Slope cover. Estimated cover system volumes with EC greater than 3 dS/m range between 1%, 7% and 10% for the Tailings 4W 60 cm, 30 cm and CTSA South Slope areas respectively. Previous monitoring at the Tailings 4W plots indicates no difference in vegetation ground cover between the 30 cm and 60 cm cover depths, but native grass species frequency was reduced in the 30 cm cover (Milczarek, 2009). It should be noted that native salt tolerant species are common in the southwestern USA, hence, loss of vegetative cover is not anticipated.

4.4 Rooting Profile Data

Observed rooting density in the Tailings 4W and SW 2 areas is presented in Table 4. Mean root size was fine or very fine at all locations with very fine roots most abundant at the 0-10 cm ac sampling position. Mean root abundance was common at 0-10 and 10-20 cm bgs under all treatments

Figure 3. Matted roots in Tailings 4W 60 cm cover material

Table 4. Rooting Density in Tailings 4W and SW2 Trenches

Cover Treatment	Average Distance to First Roots ac (cm)	Mean Root Density		
		0-10 cm bgs	10-20 cm bgs	0-10 cm ac
4W - 30 cm Cover, No Biosolids (2007)	5.2	Common	Common	Few
4W - 30 cm Cover, Biosolids (2007)	1.5	Common	Common	Common
4W - 60 cm Cover, No Biosolids (2007)	3.9	Common	Common	Few-Common
4W - 60 cm Cover, Biosolids (2007)	2.6	Common	Common	Common
SW2 - Bench 1	3.6	Common	common	Few-common
SW2 - Bench 2	3.4	Common	common	few
SW2 - Bench 4 and 5	4.3	Common	common	common

Tailings 4W trenches showed that at 0-10 cm ac, mean root density was common for biosolids-treated plots and few, or few-common, for unamended plots Table 4. Root matting was occasionally observed directly above the tailings/cover contact Table 4, in approximately one third of the trench profiles. Trench profiles at Tailings SW2 showed similar rooting density and mean root size as the unamended Tailings 4W cover plots. In general, roots within the Tailings 4W and SW2 covers extended downward until very near the tailings contact, with gravel or cobble occasionally blocking them. No roots were observed extending into tailings at either location.

Rooting to the tailings/cover contact occurred most frequently in plots that had been treated with biosolids, which also showed finer, more abundant roots and a shorter mean distance from the contact upward to the first roots. Results of ANOVA testing on the Tailings 4W rooting density results showed a significantly greater mean distance from the contact upward to first roots for the unamended biosolid plots than for the biosolids-treated plots. There were no significant differences observed in distance to the first roots between cover depths.

5 Conclusions

Depth interval sampling at four different copper mill tailings monolayer cover system sites indicates that increased salinity has occurred at all of the sites with decreased pH at two of the sites at depths of 0 to 15 cm above the tailings/cover system contact. The least significant effects were observed at the 10 year-old Tailings SW2 60 cm cover system, with high ANP cover over low pyrite tailing, and the 7 year-old CTSA Demonstration 60 cm cover system, with a high ANP cover over high pyrite tailings. The greatest effects were observed at the 10 year-old Tailings 4W 30 cm cover, and the 19-year-old 60 cm CTSA South Slope cover. Tailings 4W covers consist of moderate ANP cover over moderate pyrite tailings whereas the CTSA South Slope cover is moderate ANP over high pyrite tailings. These data indicate that the pH and EC migration may be affected by cover material neutralization potential; the strong calcareous nature of the cover material at the Tailings SW2 and CTSA Demonstration plots most likely contributed to observed minimal effects in pH and salinity above the tailings/cover contact.

The magnitude of high EC and low pH in the cover systems has been limited in space and time. The spatial variability of pH and EC affected samples was high: samples collected at similar depths in the same trench could show variation by 2 to 3 pH standard units. The Tailings 4W and South Slope area cover area showed significant mean pH and EC value effects to only 15 cm above the tailings/cover contact. Likewise, less than 25% of the samples between 0 and 15 cm above the contact in either cover system showed pH < 5. Between the 2002 and 2007 Tailings 4W sampling events there appeared to be slight decreases in EC and increases in pH within the tailings samples and cover depth samples from 5 to 15 cm above the tailings/cover contact, indicating that nominal effects on pH and EC during this 5 year period. Finally, differences in EC, pH and ANP values between the Tailings 4W cover depth treatments indicate acidity and salinity effects were greater in the 30 cm cover than the 60 cm cover at equivalent depths above the contact.

The absence of significant change in high ANP covers, observed greater effects in 30 cm cover depths than in 60 cm cover depths, observed spatial variability in iron precipitation and cover geochemical conditions indicate that the migration of infiltrating solution that has come in contact with the tailings via advection, rather than diffusion is the primary cause of decreased pH and increased EC at cover depths proximal to the tailings/cover contact. Spatial variability in geochemical conditions is consistent with expected spatial variability in cover material hydraulic properties. The conditions necessary for sufficient wetting of tailings with subsequent upward advection likely only occurs during abnormally high, summer-time, precipitation conditions. Advection of tailings solution into the cover system should be very short-term following these periods and is likely limited to a very shallow region above the tailings/cover contact. That is, as the tailings and cover system dry, the hydraulic conductivity will rapidly decrease until advection is very slow. Diffusion also becomes limited by low soil water content.

Potential effects on vegetation from lower pH and higher EC conditions at cover depths proximal to the tailings/cover contact are believed to be minor. The Tailings 4W area has been extensively monitored and ET cover performance and vegetation cover has not been negatively impacted (Milczarek, 2009). Volume calculations based on individual pH and EC values at specific depths indicate a maximum of 10% of Tailings

4W 30 cm and CTSA South Slope cover volumes are affected by pH < 5 or EC > 3 dS/m conditions, with less than 3% of the 60 cm Tailings 4W cover volume. Finally, the observed rooting characteristics indicate that the ability of these shallow covers to support vegetation does not appear to be compromised.

The long-term fate of shallow monolayer cover systems is likely dependent on the cover material texture, ANP, and underlying tailings pH and pyrite conditions. In the case of moderate to high ANP covers, advection of tailings solution into the cover during these periods should result in acid neutralization and ongoing rinsing of the upper portions of the cover from infiltration should minimize EC concentration at all but the proximal regions to the tailings/cover contact. Cover systems less than 30 cm in depth can expect to potentially experience greater advection due to greater wetting and greater hydraulic gradients due to the relatively short distance from the surface to the tailings/cover contact. In the case of the CTSA Demonstration and Tailings SW2, high ANP covers may be sufficient to maintain high pH conditions indefinitely. The Tailings 4W and CTSA South Slope areas may expect an increase in the spatial distribution of acidity and EC affected soil between 0 and 15 cm ac, but may not experience any additional salinization above 15 cm. In any case, upward migration of tailings solution and mixing of materials appears to occur around the contact zone. These and other study results (i.e. Milczarek 2009, Munk, 2006), indicate that upward migration in up to 15 cm of cover material directly above the tailings/cover contact for periods of up to 19 years, has not negatively affected vegetative cover, rooting dynamics, or ET performance over a range of ET cover systems and varying tailings chemistries in semiarid climates of the southwest.

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