Report on Characterization of Waste Rock and Tail ings Piles Above Creede, Col orado



FINAL

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Introduction

Willow Creek, formed by the confluence of East and West Willow Creeks, is a tributary of the Rio Grande River near its headwaters in the San Juan Mountains in Mineral County, Colorado. Historic mining activities related to underground mining of silver and selected base metals resulted in significant water quality impairment in the 35 square mile Willow Creek watershed (zinc, cadmium and lead exceed the Colorado Table Value Standards). The State of Colorado has placed this segment of the Rio Grande River on their Clean Water Act 303(d) list. The residents of the town of Creede and the surrounding portion of Mineral County have developed a community-based effort to identify and address the most pressing environmental concerns in the Willow Creek watershed. The Willow Creek Reclamation Committee (WCRC), convened in 1999, is directing a stakeholder effort aimed at improving water quality and physical habitat in the Willow Creek watershed as part of a long-term watershed management program which will focus on restoring aquatic resources and protecting the Rio Grande from future fish kills.

From 1999 through 2003, the WCRC, with technical and financial assistance from the US Environmental Protection Agency, the United States Forest Service, the Natural Resources Conservation Service, the Colorado Division of Minerals and Geology and the Colorado Department of Public Health and Environment, has directed a variety of watershed characterization efforts. These efforts have been aimed at:

- (1) Identifying sources of heavy metals
- (2) Characterizing transport of heavy metals to surface waters
- (3) Quantifying heavy metals loading to Willow Creek and the Rio Grande River
- (4) Characterizing mine waste materials
- (5) Biological assessment of aquatic resources
- (6) Characterizing hydrological conditions in underground mine workings

The findings and conclusions from these characterization efforts are summarized in a series of five reports prepared by the Technical Advisory Committee of the WCRC. These reports include:

- (1) Report on Surface and Groundwater Sampling and Monitoring in Willow Creek Watershed, Mineral County, CO (1999-2002)
- (2) Report on Characterization of Groundwater in the Alluvial Deposits beneath the Floodplain of Willow Creek below Creede
- (3) Report on Characterization of Waste Rock and Tailings Piles above Creede, Colorado
- (4) Report on Characterization of Fish and Aquatic Macroinvertebrates in Willow Creek
- (5) Evaluation of Metal Loading to Streams near Creede, Colorado

These reports will provide the basis for choosing the remedial actions that will be evaluated (in terms of engineering and economic feasibility) for identifying and implementing watershed restoration activities.

This report presents the results of characterization of tailings and waste rock piles in the Willow Creek watershed. The objective was to ascertain the type, degree, and extent of contamination of surface and shallow depth soils/sediments.

Materials and Methods

Due to historic silver mining, many tailings and waste rock piles exist in the Willow Creek Watershed. Heavy metals leached from the rock via infiltration of snow and rain have migrated and resulted in contamination of surface water and/or groundwater. Erosion and acidic runoff have also resulted in vegetational kill zones on and around some of the piles. The Sampling and Analysis Plan for Tailings, Waste Rock Piles, and Floodplain Sediment (2001) is attached as Appendix A.

Site Selection

A map of the sampled waste rock and tailings piles is shown in Figure 1. Waste rock samples were collected September 18-20, 2001, for all sites except Happy Thought and Last Chance. These two sites were sampled on August 16, 2002. In the field, individual waste rock and tailings piles were visually divided into roughly homogeneous strata based on features such as color and texture (see Appendix A). Maps were created in the field that identified strata boundaries, properties of the strata, and other landscape features. Photographs were taken to compliment hand-drawn maps. Photographs showing strata locations and characteristics for each waste rock/tailings pile are included in Appendix B.

Sample Collection

Up to 30 random samples were collected from each stratum to create a Surface Grab Composite (SGC). When a stratum was present as two or more separate areas, samples were collected from each of the areas in numbers proportional to the relative size of the area. Grab samples were obtained by using a new plastic cup to scoop the surface and top few centimeters of material. Grab samples from a given stratum were composited in an appropriately labeled Ziploc[™] bag. Depth samples were collected from a depth of 1.5 to 3 feet, depending on the material and slope of the area. Depth samples were placed in appropriately labeled Ziploc[™] bags. Labels were also created on Rite in the Rain[™] paper and placed inside the bags. All samples were double-bagged for transport and shipment to the laboratory.

Paste pH and Conductivity

Surface composites and depth samples were analyzed for paste pH and conductivity at each site. Methods for paste analyses were derived from those of Robertson Geoconsultants Inc. (see Appendix A). Prior to analyses, probes were calibrated according to the manufacturer's directions. Approximately 2 tablespoons of sample (preferably fine material) were mixed with 2 tablespoons of deionized water in a new plastic cup. Samples were stirred for approximately 30 seconds to create a slurry. Probes were inserted into the slurry, and readings were allowed to stabilize before being recorded. Probes were thoroughly rinsed with deionized water and wiped clean of any residue between samples. For some of the samples, pH papers were used for comparison with the meter, but staining from the slurry made readings difficult.

Acidity and Metal Extraction

Initially, an attempt was made to perform the water extraction as described in the SAP (Appendix A). Due to difficulty with filtration on site, dry samples were sent to ACZ Laboratory (Steamboat Springs, CO) for processing. Procedures for extraction followed EPA Method ASA No. 9, 10-2.3.2. The procedure was modified to a 2:1 liquid (deionized water) to solid ratio in accordance with an approach recommended by the State of Colorado's Division of Minerals and Geology. Samples were analyzed for acidity (as CaCO₃), arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn). All samples were analyzed within the holding limits for the given methods and parameters.

Toxicity Characteristic Leaching Procedure

Based on the laboratory results from the water extractions, several sites were selected that had high levels of one or more water-extractable metals. These sites were re-sampled on August 16, 2002, by the methods described above. Samples were shipped to ACZ laboratories for analysis using the Toxicity Characteristic Leaching Procedure (TCLP). Metals evaluated with TCLP were arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), selenium (Se), silver (Ag), and zinc (Zn).

Results

Paste pH and conductivity

Table 1 presents data derived from paste analyses for conductivity and pH. Conductivity and temperature values are shown in Figure 2. Average conductivity values ranged from 5 μ S/cm at the Amethyst Stratum B, to 3346 μ S/cm at Last Chance Stratum E. Paste conductivities from sites at the

Commodore, Happy Thought, Last Chance, Midwest, and Park Regent were higher than at the other sites. Values of pH are shown in Figure 3. Low pH values (2 - 3) were found at the Midwest (2.0, 2.6) and Park Regent (2.6, 2.9). Values close to neutral (6 - 8) were measured in samples from the Gormax (6.7, 7.0); Happy Thought Stratum C (8.2); Last Chance Depth (6.5) and Stratum D (6.3); Outlet Stratum C (6.9); and Solomon Stratum B (6.0) and Depths #1 and #2 (6.8, 6.9).

Acidity and Metal Extraction

Data derived from the 2:1 deionized water extractions are presented in Table 2. Samples at each site were collected either as a Surface Grab Composite (SGC) or at Depth as described in Materials and Methods. Acidity values (mg CaCO₃/kg of sample) are shown in Figure 4. High acidity values should correlate to a low pH for a given samples. Samples from the Gormax and Phoenix Mine sites had consistently high levels of acidity (1690 - 7390 mg CaCO₃/kg). Sites at the Last Chance were generally the lowest in acidity (range: <2 - 244 mg CaCO₃/kg), with the exception of Stratum E (1940 mg CaCO₃/kg).

Arsenic levels in waste rock samples were generally less than 0.1 mg As/kg, as shown in Figure 5. Sites with the highest levels of arsenic were the Bachelor 2 (0.15-0.19 mg As/kg), Midwest (0.06-1.16 mg As/kg), and Outlet (0.05-0.44 mg As/kg). The lowest arsenic values (<0.013 mg As/kg) were noted for the Bachelor 1, Happy Thought, Last Chance, Phoenix Mill, and Solomon. Cadmium values were highly variable within and among sites (Figure 6). Maximum cadmium values were found at the Happy Thought Stratum A (8.08 mg Cd/kg) and Last Chance Stratum E (7.87 mg Cd/kg). All other samples were below 2 mg Cd/kg, with values below the limit of detection (0.006 mg Cd/kg) determined for the Gormax and small piles at the Midwest, Outlet, and Park Regent.

The maximum copper value, obtained from a small pile at the Commodore, was 18.9 mg Cu/kg, more then five times the levels found at the other sites (Figure 7). Several areas at the Amethyst, Bachelor 1, Commodore, and Park Regent had copper levels above 1 mg Cu/kg. The lowest copper levels (<0.2 mg Cu/kg) were found at the Gormax, Phoenix Mine, Phoenix Mill, and the Solomon. Lead values from deionized water extractions are shown in Figure 8. Maximum lead concentrations were found at the Amethyst Stratum A (21.40 mg Pb/kg), Amethyst Stratum C (20.90 mg Pb/kg), Last Chance Stratum C (19.90 mg Pb/kg), and Ridge Stratum A (27.50 mg Pb/kg). Overall, lead levels were the lowest (<0.33 mg Pb/kg) at the Gormax and Midwest sites.

Zinc levels were the highest and most variable at the Happy Thought (min. 18.5 mg Zn/kg; max. 1020.0 mg Zn/kg) and the Last Chance (min. 0.4 mg Zn/kg; max. 1290.0 mg Zn/kg). All other sites had values below 200 mg Zn/kg,

with half of the sites below 15 mg Zn/kg. Samples from the Gormax, Holy Moses, Midwest, Outlet, and Phoenix Mine had the lowest zinc levels.

Toxicity Characteristic Leaching Procedure

Sites that were selected for analysis by TCLP are listed along with the results in Table 3. Although mine waste is exempt from the Resource Conservation and Recovery Act (RCRA) standards, these standards are presented as a basis of comparison. Overall, levels of arsenic, chromium, mercury, selenium, and silver were near or below the Method Detection Limit as determined by the laboratory, and therefore will not be further discussed. Barium values ranged from 0.003 to 0.217 mg/L, which were less than 1% of RCRA standards. For the remaining metals, cadmium, copper, lead, and zinc, the Happy Thought and Last Chances piles had the greatest values.

Cadmium levels from TCLP are presented in Figure 10. All sites were below the RCRA standard of 1 mg Cd/L, and the highest levels were noted for Happy Thought Stratum A (0.82 mg Cd/L) and Last Chance Stratum E (0.74 mg Cd/L). Copper values (Figure 11) were generally below 0.3 mg Cu/L, with the exception of Happy Thought Depth (0.96 mg Cu/L) and Stratum A (1.8 mg Cu/L) and Last Chance Stratum E (1.4 mg Cu/L).

Lead values (Figure 12) ranged from 0.2 to 252 mg Pb/L, and were all well over the RCRA standard (5 mg Pb/L). TCLP data indicated that the highest levels of zinc (Figure 13) were at the Happy Thought Depth (162 mg Zn/L) and Stratum A (128 mg Zn/L) and the Last Chance Stratum E (241 mg Zn/L).

Site Specific Summaries

Amethyst-	Leachate from the Amethyst samples was mildly acidic. Heavy metals were mid-range for all samples collected, with slightly higher levels of copper and lead.
Bachelor 1&2-	Leachate from Bachelor samples was mildly acidic with relatively low conductivities. Heavy metals were mid-range for all samples collected, with slightly higher levels of copper and lead.
Commodore-	Leachate from the Commodore samples was slightly acidic, with relatively high conductivities from the three strata. Extractable metals were also higher in general than the other sites, especially in terms of copper, cadmium and zinc.
Gormax-	Leachate from the Gormax samples was near neutral with low conductivity. Acidity as CaCO ₃ was relatively high, but extractable metals were lower than most sites.

- Happy Thought- Leachate from the Happy Thought samples was slightly acidic to neutral, with high conductivities in Depth, Stratum A, and Stratum C samples. Metals were average to below average, with the exception of cadmium and zinc. Stratum A was high in leachable metals as indicated by TCLP. As shown by the photos, Stratum A is grey material near the top of the pile. The Depth sample TCLP data indicate that high leachability of metals is not limited to the surface materials. Stratum C is highly erodable, fine material near the bottom of the pile. Due to its proximity to the stream, Stratum C could be a source of zinc and cadmium contamination to West Willow Creek.
- Holy Moses-Leachate from the Holy Moses samples was slightly acidic with low conductivities. Metals were at or below the average for all sites, and the surface might be a greater source of cadmium and lead than deeper material.
- Last Chance-Leachate from the Last Chance samples was slightly acidic with a range of conductivities. Stratum E had the highest conductivity and leachable zinc of all sites. Cadmium from Stratum E was also greater than all sites but Happy Thought Stratum A. Last Chance Stratum A had elevated levels of cadmium and zinc. The Depth and Stratum D samples had metal levels below average, and Strata B and C were close to average. Based on the location of the strata, it appears that the cadmium and zinc were associated with grey material found near the top of the pile.
- Midwest-Leachate from the Midwest samples was acidic with relatively high conductivities. Arsenic and acidity are the primary problems with this site.
- Outlet-Leachate from the Outlet samples was acidic in Depth and Stratum A and B samples, but near neutral in Stratum C. Conductivities were at or below average. Metals were generally below average, with the exception of arsenic.
- Park Regent-Leachate from the Park Regent samples was acidic with midrange conductivities. Metals were close to average, with elevated copper levels in Depth and surface samples.
- Phoenix Mine- Leachate from the Phoenix Mine samples was slightly acidic with very low conductivities. Acidities as CaCO₃ in Depth and

both Strata samples were above all other sites. Metals were generally below average.

- Phoenix Mill-Leachate from Phoenix Mill samples was slightly acidic with mid-range conductivities. Extractable metals were near the average for all sites.
- Ridge-Leachate from the Ridge samples was slightly acidic with midrange conductivities. Stratum A had high levels of lead. Other metals were average, and there were no substantial differences between depth and surface samples.
- Solomon-Leachate from the Solomon samples was slightly acidic with mid-range conductivities. Levels of extractable metals were average to above average, with slightly higher values in the Depth samples as compared to the Strata.

Discussion and Conclusions

Based on the paste conductivity and pH analyses, it can be determined that although these procedures can indicate gross differences among sites, variability among subsamples makes precise measurements and replication difficult. Data from paste pH and laboratory acidity analyses were not comparable and indicated different sites as acid producers. Paste conductivities corresponded closely with water extraction results for cadmium and zinc (r^2 >0.6), but not for arsenic, copper, or lead. Paste conductivities may provide the best means of determining heavy metal leaching potential without sending a sample to a laboratory.

Overall, there was not a substantial difference between depth and surface samples. These piles are relatively homogeneous within the top couple of feet. Deeper sampling might be necessary to determine if the lower portions of the piles are more easily leached.

These data provide an indication of which sites are the greatest potential contributors of acid or heavy metal contamination to ground and surface water; however, other factors such as volume of waste rock, run-on/run-off, erosion, and proximity to water also determine the potential for surface/ground water contamination. Table 4 presents a ranking of sites that takes into consideration laboratory results, erosion potential, and location. This evaluation identified the Park Regent, Ridge, Amethyst, and Phoenix Mine as the top four sites in terms of contamination potential. It should also be noted that the Happy Thought and the Last Chance were also possible heavy metal sources as indicated by the 2:1 and TCLP extractions. The future development of remediation efforts will need to be site-specific and will require evaluation of these data and all other factors.

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Table 1. Paste data for conductivity, temperature, and pH. Values from composites are presented as the average +/- 1 standard deviation from the mean of 5 samples. Values derived with pH paper are presented as the range of five samples.

				Paste			
				Conductivity			рΗ
Waste Pile	Туре	Date	Time	(µS/cm)	at Temp	pH meter	paper
Amethyst	Depth 23"	9/20/2001	1440	275	17.6	3.4	4.3
Amethyst	Stratum A	9/20/2001	1330	134 +/- 90	17.5 +/- 0.3	3.7 +/- 0.4	4.0-4.3
Amethyst	Stratum B	9/20/2001	1400	5 +/- 2	16.9 +/- 0.7	5.9 +/- 0.5	4.3-5.0
Amethyst	Stratum C	9/20/2001	1430	181 +/- 169	17.9 +/- 0.5	3.9 +/- 0.4	3.7-4.3
Bachelor 1	Depth	9/19/2001	1155	312	19.4	3.8	4-5
Bachelor 1	N Stratum	9/19/2001	1145	60 +/- 32	19.2 +/- 0.4	3.8 +/- 0.3	3-4
Bachelor 1	S Stratum	9/19/2001	1200	60 +/- 25	19.6 +/- 0.4	3.7 +/- 0.1	4-5
Bachelor 2	Depth	9/19/2001	1057	43	20.1	5.3	5-6
Bachelor 2	Only Stratum	9/19/2001	1100	69 +/- 28	19.0 +/- 0.4	5.0 +/- 0.5	4-6
Commodore	Depth 32"	9/19/2001	1508	112	18.3	5.5	5
Commodore	M Stratum	9/19/2001	1530	803 +/- 992	19.3 +/- 0.4	3.8 +/- 0.4	3-5
Commodore	N Stratum	9/19/2001	1440	697 +/- 433	19.7 +/- 0.7	3.8 +/- 1.3	2-6
Commodore	S Stratum	9/19/2001	1500	574 +/- 603	18.8 +/- 0.8	4.5 +/- 0.7	3-6
Gormax	Depth	9/18/2001	1120	24	18.3	7.0	
Gormax	Only Stratum	9/18/2001	1120	113 +/- 208	20.4 +/- 0.4	6.7 +/- 0.5	5.0-5.7
Happy Thought	Depth 2'	8/16/2002	1145	567	22.6	5.9	
Happy Thought	Stratum A	8/16/2002	1145	2500 +/- 57	22.2 +/- 0.1	5.2 +/- 0.1	
Happy Thought	Stratum B	8/16/2002	1145	114 +/- 18	22.1 +/- 0.1	4.0 +/- 0.0	
Happy Thought	Stratum C	8/16/2002	1145	792 +/- 75	25.0 +/- 0.2	8.2 +/- 0.2	
Holy Moses	Depth 3'	9/19/2001	1000	23	18.0	5.7	4.5
Holy Moses	Only Stratum	9/19/2001	1000	41 +/- 21	18.3 +/- 0.3	4.5 +/- 0.9	4.3-4.5
Last Chance	Depth 1.5'	8/16/2002	930	104	22.4	6.5	
Last Chance	Stratum A	8/16/2002	930	340 +/- 12	21.8 +/- 0.4	5.6 +/- 0.1	
Last Chance	Stratum B	8/16/2002	930	124 +/- 5	21.9 +/- 0.1	4.4 +/- 0.1	
Last Chance	Stratum C	8/16/2002	930	88 +/- 6	22.5 +/- 0.1	4.1 +/- 0.0	
Last Chance	Stratum D	8/16/2002	930	544 +/- 39	22.4 +/- 0.2	6.3 +/- 0.1	
Last Chance	Stratum E	8/16/2002	930	3346 +/- 324	22.4 +/- 0.1	5.7 +/- 0.0	
Midwest	Depth	9/19/2001	1615	2520	19.9	2.0	2-3
Midwest	Only Stratum	9/19/2001	1615	406 +/- 445	19.0 +/- 1.0	2.6 +/- 0.7	2-4
Outlet	Depth 21"	9/18/2001	1400	76	17.60	3.25	3-4
Outlet	Stratum A	9/18/2001	1400	278 +/- 169	15.9 +/- 2.0	3.2 +/- 0.6	2-4
Outlet	Stratum B	9/18/2001	1400	115 +/- 82	16.4 +/- 0.8	4.4 +/- 1.0	3-6
Outlet	Stratum C	9/18/2001	1400	73 +/- 49	16.7 +/- 0.8	6.9 +/- 0.7	5-7
Park Regent	Depth	9/19/2001	1645	720	19.4	2.6	3
Park Regent	Only Stratum	9/19/2001	1650	459 +/- 478	18.8 +/- 0.8	2.9 +/- 0.7	2-4
Phoenix Mine	Depth 2'	9/18/2001		19	19.1	5.6	
Phoenix Mine	Lower Stratum	9/18/2001	1150	22 +/- 11	19.5 +/- 0.6	5.7 +/- 0.4	4.0-5.1
Phoenix Mine	Upper Stratum	9/18/2001	1150	23 +/- 3	19.8 +/- 0.6	5.5 +/- 0.6	5-6
Phoenix Mill	Only Stratum	9/18/2001	1020	402 +/- 281	17.8 +/- 0.9	5.5 +/- 0.2	4-7
Phoenix Mill	Depth 24"	9/18/2001	1020	368	16.9	5.5	4-5
Ridge	Stratum A	9/19/2001	1600	220 +/- 229	19.1 +/- 1.1	4.6 +/- 0.6	3-5
Ridge	Stratum B	9/19/2001	1530	220 +/- 238	18.1 +/- 0.5	5.5 +/- 0.4	4.3-5.4
Solomon	Stratum A	9/20/2001	1200	133 +/- 99	18.1 +/- 0.7	5.1 +/- 0.3	4.3-4.5
Solomon	Stratum B	9/20/2001	1155	145 +/- 53	17.2 +/- 0.8	6.0 +/- 0.1	4.3-4.5
Solomon	Stratum C	9/20/2001	1208	289 +/- 164	17.5 +/- 0.6	5.5 +/- 0.8	4.3-4.5
Solomon	Depth #1	8/16/2002	1513	150	25.6	6.8	
Solomon	Depth #2	8/16/2002	1513	176	25.3	6.9	
Solomon	Stratum B Depth 32"	9/20/2001	1200	257	17.3	5.0	4.3

Table 2. Data from 2:1 extraction with deionized water. Sample types were Surface Grab Composites (SGC) or Depth samples.Boldface indicates values were below the Practical Quantitation Limits. Values with "<" were below the Method Detection Limit. Acidity is as $CaCO_3$.

			Acidity	As	Cd	Cu	Pb	Zn
Waste Pile	Туре	Date	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Amethyst	Depth 23"	9/20/2001	778	0.011	0.287	1.21	12.30	21.3
Amethyst	Stratum A SGC	9/20/2001	466	0.008	0.145	2.18	21.40	11.7
Amethyst	Stratum B SGC	9/20/2001	749	0.023	0.070	0.11	1.70	2.7
Amethyst	Stratum C SGC	9/20/2001	408	0.007	0.243	0.49	20.90	16.2
Bachelor 1	Depth	9/19/2001	300	0.011	0.405	2.00	7.13	30.6
Bachelor 1	N Stratum SGC	9/19/2001	508	0.005	0.417	1.45	14.10	31.0
Bachelor 1	S Stratum SGC	9/19/2001	549	0.003	0.074	0.78	9.83	2.9
Bachelor 2	Depth	9/19/2001	674	0.190	0.139	1.04	5.90	10.9
Bachelor 2	SGC	9/19/2001	574	0.148	0.056	0.30	2.37	5.3
Commodore	#2 North (small) SGC	9/19/2001	882	0.091	0.661	18.90	6.49	97.3
Commodore	Depth 32"	9/19/2001	420	0.000	0.259	0.47	10.70	33.6
Commodore	M Stratum SGC	9/19/2001	582	0.000	0.867	1.55	6.10	117.0
Commodore	N Stratum SGC	9/19/2001	441	0.004	0.648	1.53	9.74	87.6
Commodore	S Stratum SGC	9/19/2001	574	0.007	1.080	1.79	8.96	177.0
Gormax	Depth	9/18/2001	4180	0.049	<0.006	<0.02	<0.08	2.1
Gormax	SGC	9/18/2001	1690	0.025	<0.006	<0.02	0.25	1.1
Happy Thought	Depth 2'	8/16/2002	503	<0.002	1.730	<0.10	2.30	291.0
Happy Thought	Stratum A SGC	8/16/2002	1600	0.002	8.080	1.10	1.30	1020.0
Happy Thought	Stratum B SGC	8/16/2002	40	0.011	0.130	0.19	7.35	18.5
Happy Thought	Stratum C SGC	8/16/2002	359	<0.002	1.510	0.20	5.10	240.0
Holv Moses	Depth 3'	9/19/2001	603	0.078	0.017	0.05	<0.08	2.7
Holy Moses	SGC	9/19/2001	499	0.025	0.344	0.25	12.10	2.3
Last Chance	Depth 1.5'	8/16/2002	<2	0.013	<0.01	<0.02	0.28	0.4
Last Chance	Stratum A SGC	8/16/2002	244	<0.002	1.130	<0.10	3.50	149.0
Last Chance	Stratum B SGC	8/16/2002	39	0.003	0.210	0.44	6.66	15.9
Last Chance	Stratum C SGC	8/16/2002	48	<0.002	0.180	0.81	19.90	4.7
Last Chance	Stratum D SGC	8/16/2002	<2	<0.002	0.110	<0.02	0.10	3.6
Last Chance	Stratum E SGC	8/16/2002	1940	0.003	7.870	0.20	1.80	1290.0
Midwest	Depth	9/19/2001	1410	1.160	0.127	1.03	<0.08	5.4
Midwest	SGC	9/19/2001	599	0.059	0.012	0.08	<0.08	1.6
Midwest #1	(small) SGC	9/20/2001	886	0.770	0.011	0.27	0.33	2.2
Midwest #2	(small) SGC	9/19/2001	354	0.056	<0.006	<0.02	<0.08	0.6
Outlet	Depth 21"	9/18/2001	420	0.056	0.015	0.07	0.44	2.4
Outlet	Stratum A #5 (sm) SGC	9/18/2001	424	0.437	<0.006	0.03	0.10	1.0
Outlet	Stratum A SGC	9/18/2001	441	0.095	0.071	1.33	0.15	2.6
Outlet	Stratum B SGC	9/18/2001	537	0.045	0.090	0.22	9.28	1.7
Outlet	Stratum C SGC	9/18/2001	1460	0.180	0.009	0.04	0.34	2.4
Park Regent	#5 (sm) SGC	9/19/2001	574	0.069	<0.006	0.07	1.04	1.4
Park Regent	Depth	9/19/2001	811	0.028	0.219	2.88	9.92	31.2
Park Regent	SGC	9/19/2001	1110	0.075	0.645	2.97	8.12	81.9
Phoenix Mine	Depth 2'	9/18/2001	5610	0.075	0.017	0.03	0.45	3.5
Phoenix Mine	Lower Stratum SGC	9/18/2001	4180	0.109	0.015	<0.02	0.16	2.7
Phoenix Mine	Upper Stratum SGC	9/18/2001	7390	0.105	0.120	0.14	8.85	3.5
Phoenix Mill	SGC	9/18/2001	404	0.007	0.477	0.04	6.17	52.6
Ridae	Depth 24"	9/19/2001	508	<0.002	0.609	0.16	9.94	87.4
Ridae	Stratum A SGC	9/19/2001	1360	0.032	0.523	0.34	27.50	69.9
Ridae	Stratum B SGC	9/19/2001	691	0.004	0.680	0.07	5.73	80.6
Solomon	Stratum B Depth 32"	9/20/2001	815	0.004	0.779	0.16	15.10	93.5

Table 2. (Continued)

Waste Pile	Туре	Date	Acidity (mg/kg)	As (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Solomon	Stratum A SGC	9/20/2001	599	0.003	0.412	0.07	13.70	44.7
Solomon	Stratum B SGC	9/20/2001	765	0.002	0.340	0.04	8.64	27.1
Solomon	Stratum C SGC	9/20/2001	578	0.005	0.503	0.03	9.60	48.8
Solomon	Pond #1 SGC	9/20/2001	408	0.013	0.010	<0.02	0.22	0.6

Table 3. TCLP results from samples collected 8/16/02. Boldface indicates values were below the Practical Quantitation Limit (PQL) as determined by ACZ Laboratories. Values in () indicate PQL for that sample dilution. Values below the Method Detection Limit (MDL) are shown as less than the applicable MDL for that sample dilution. Resource Conservation and Recovery Act (RCRA) standards have not been established for copper and zinc.

Waste Pile	Туре	TCLP As	TCLP Ba	TCLP Cd	TCLP Cr	TCLP Cu	TCLP Pb	TCLP Hg	TCLP Se	TCLP Ag	TCLP Zn
		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Commodore	Pile A SGC	<0.04	0.053	0.116	<0.01	0.12	92	<0.0002	<0.08	<0.005	16.5
Commodore	Stratum B SGC	<0.04	0.027	0.157	<0.01	0.04 (0.05)	46	<0.0002	<0.04	0.007 (0.03)	21.5
Commodore	Stratum C SGC	<0.04	0.217	0.178	<0.01	0.26	110	<0.0002	<0.04	<0.005	31.0
Happy Thought	Depth	<0.04	0.005 (0.01)	0.498	0.01 (0.05)	0.96	224	<0.0002	<0.04	<0.3	162.0
Happy Thought	Stratum A SGC	0.05 (0.2)	0.005 (0.01)	0.820	<0.01	1.80	167	<0.0002	<0.04	<0.3	128.0
Last Chance	Stratum E SGC	<2	<0.2	0.740	<0.1	1.40	252	<0.0002	<0.4	<0.3	241.0
Park Regent	SGC	<0.04	0.089	0.084	<0.01	0.07	64	<0.0002	<0.04	0.007 (0.03)	10.2
Ridge	Stratum A SGC	<0.04	0.012 (0.02)	0.409	<0.01	0.05 (0.1)	131	<0.0002	<0.04	<0.005	42.0
	Depth #1 (Stratum B Site										
Solomon	1)	<0.04	0.073	0.109	<0.01	0.22	80	<0.0002	<0.04	<0.005	17.2
	Depth #2 (Stratum B Site										
Solomon	2)	<0.04	0.037	0.188	<0.01	<0.02	102	<0.0002	<0.04	<0.005	19.8
Solomon	Stratum A SGC	<0.04	0.019 (0.02)	0.224	<0.01	<0.02	144	<0.0002	<0.04	<0.005	30.7
RCRA Sta	andards (mg/L)	5	100	1	5	-	5	0.2	1	5	-

Site	Acidity Rank	Metal Rank	Location Rating ^a	Erosion Rating ^D	Overall Rank
Park Regent	3	4	4	1	1
Ridge	4	3	2	4	2
Amethyst	7	5	1	3	3
Phoenix Mine	1	12	2	1	3
Commodore	11	1	1	4	5
Solomon	6	6	2	3	5
Bachelor	10	2	4	4	7
Midwest	5	13	1	1	7
Holy Moses	7	10	3	1	9
Gormax	2	14	4	3	10
Outlet	9	9	2	4	11
Happy Thought	12	7	4	3	12
Last Chance	13	11	2	2	13
Phoenix Mill	14	8	3	4	14

Table 4. Prioritization of sites based on a ranking of acidity, metals, location, and erosion.

a. Basis for location rating: 1= in a perennial or intermittent stream; 2= in an ephemeral stream or near an intermittent or perennial stream; 3= 25-100 yards from a stream; 4= >100 yards from a stream.

b. Basis for erosion rating: 1= gullies over 12 inches deep; 2= gullies 6-12 inches deep; 3= rill erosion; 4= no erosion or sheet flow erosion.

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Figure 2. Paste conductivity of waste rock piles. Data are presented as the average of five samples for each stratum. Error bars represent one standard deviation above and below the mean. Crosses represent sample temperatures at the time of analysis.



Figure 3. Paste conductivity of waste rock piles. Data are presented as the average of five samples for each stratum. Error bars represent one standard deviation above and below the mean.



Figure 4. Acidity of waste rock piles as determined by 2:1 extraction with deionized water. Sites are divided into Surface Grab Samples (SGC) and Depth Samples. Acidity is expressed as mg CaCO₃/kg.



Figure 5. Arsenic in waste rock piles as determined by 2:1 extraction with deionized water. Sites are divided into Surface Grab Samples (SGC) and Depth Samples.



Figure 6. Cadmium in waste rock piles as determined by 2:1 extraction with deionized water. Sites are divided into Surface Grab Samples (SGC) and Depth Samples.



Figure 7. Copper in waste rock piles as determined by 2:1 extraction with deionized water. Sites are divided into Surface Grab Samples (SGC) and Depth Samples.



Figure 8. Lead in waste rock piles as determined by 2:1 extraction with deionized water. Sites are divided into Surface Grab Samples (SGC) and Depth Samples.



Figure 9. Zinc in waste rock piles as determined by 2:1 extraction with deionized water. Sites are divided into Surface Grab Samples (SGC) and Depth Samples.



Figure 10. Data from TCLP analysis for cadmium. Samples were identified by the 2:1 extractions as having elevated metal concentrations.



Figure 11. Data from TCLP analysis for copper. Samples were identified by the 2:1 extractions as having elevated metal concentrations.



Figure 12. Data from TCLP analysis for lead. Samples were identified by the 2:1 extractions as having elevated metal concentrations.



Figure 13. Data from TCLP analysis for zinc. Samples were identified by the 2:1 extractions as having elevated metal concentrations.

APPENDIX A

SAMPLING AND ANALYSIS PLAN

Waste Rock Sampling

This SAP is for Phase I screening of waste rock piles, tailings, and floodplain sediment in the Willow Creek drainage. A rigorous statistical resolution of contamination levels or of core drilling of the tailing piles is not presently included in the protocol. The purpose of Phase I is to narrow down the areas of concern and areas of highest priority for more extensive examination. Future detailed analyses, if necessary, may be addressed by an update to this SAP.

The purpose of this SAP is to describe the equipment and operations used for sampling surface and shallow depth soils. The objective is to ascertain the type, degree, and extent of soil contamination at a site according to a first pass low resolution and narrowing down of priority areas. The data can then be used to evaluate potential threats to human health or the environment, to evaluate potential exposure pathways, or to calculate environmental risks and allow the Willow Creek Reclamation Committee (WCRC) to focus on areas of highest concern.

This SAP outlines methods for soil sampling with routine field operations on WCRC projects. Sitespecific deviations from the methods presented herein must be approved by the WCRC Technical Advisory Committee (TAC) and/or noted on datasheets for presentation to the QAQC manager. The project leader at the field site checks all exhibits and field log books for completeness and accuracy. Any discrepancies are noted and the documents are returned to the originator for correction. Each sampling includes the appropriate number of samples for statistical analysis, duplicate samples, and blanks.

Soil samples gathered in accordance with this SAP are analyzed for concentrations of lead, arsenic, cadmium, and zinc by Trace ICP according to the procedures in SW-846, 3rd edition, Method Number 6010B. Soil sample digestion is by method 3050B.

1. Source Area Sample Site Locations

Lack of homogeneity in sampling is the single biggest source of error in sampling waste dumps and is called the fundamental error. This concept is important and could have large impacts on remediation options related to both expense and procedure. Because the mine waste rock piles, tailing, and floodplain sediment areas (i.e. potential source areas) are relatively large and diverse, each of the areas is separated into homogeneous units as described below.

Although it is likely that in many cases what is seen on the surface is similar to how it is at depth within the parent material, it is reasonable to expect that the material may also change dramatically with depth. To provide a screening level evaluation of the areas, each of the potential source areas is separated and mapped by rough units of general surface homogeneity by viewing features such as color, texture, and other surface features that may indicate similar material. In addition, aerial photography, if available, may be used to identify the homogeneous units within these potential source areas. Based on the visual observations, a sketch map of the homogeneous units is developed for each of the potential source areas. Each homogeneous unit is then sampled in accordance with Section 2.

2. Sample Collection

Once the homogeneous units within each potential source area are identified and mapped, three different types of samples are collected within each homogeneous unit. The samples to be collected include:

- Surface composite samples representative of each homogeneous unit,
- Surface samples within each homogeneous unit, and

• Depth samples within each potential source area.

<u>Surface Composite Samples</u>: At each homogeneous unit identified within a potential source area (waste pile, tailing, floodplain sediment), a total of thirty (30) random surface (0-4 inches) samples will be gathered. A smaller number of samples may be collected based on unit size or field conditions. These samples are located such that they provide a representative composite of the homogeneous unit. At each location, a plastic cup or clean trowel (See Section 8) is used to scoop a surface sample into a designated large (e.g. Gallon size) Ziploc bag for the composite sample. Once the surface samples have been gathered into the composited Ziploc bag, it is double bagged and labeled to indicate the location, date, sampler's initials, and remarks, if any.

<u>Surface Samples</u>: In addition to the composite sample described above, at five (5) of the thirty locations used for a composite in each homogeneous unit, an additional surface sample may be gathered. These five locations are representative of the homogeneous unit. At each location, a plastic cup or decontaminated trowel (See Section 8) is used to scoop the surface sample into a new designated large (e.g. Gallon size) Ziploc bag. Once the surface samples have been gathered, each is double bagged and labeled to indicate the location, date, sampler's initials, and remarks, if any.

<u>Depth Samples</u>: At each potential source area (i.e. waste pile, tailing, and floodplain sediment), one depth sample is gathered. Each depth sample is obtained by digging into the pile area with a clean shovel (See Section 8). The location of the depth sample is such that it best represents the source area based on field visual observations. The target depth for each sample is four (4) feet, depending on the percent slope, soil texture conditions. Care is taken to ensure that the upper materials do not contaminate the material to be sampled at depth. The depth sample is then placed in a new Ziploc bag. Once the depth samples have been gathered, each is double bagged and labeled to indicate the location, date, sampler's initials, and remarks, if any.

3 Field Paste pH and Conductivity

For each soil sample gathered as described above, a field paste pH and conductivity analysis is performed. The analysis is performed according to the Robertson Geoconsultants Inc. Method, as presented in Appendix A.

4 Laboratory Analysis

In addition to the field paste pH and conductivity analysis, each of the soil samples gathered is packaged, labeled, and shipped (See Sections 5 and 6) to a designated laboratory for the following analysis:

- Leaching/Water Extraction for Metals Analysis (EPA Method ASA No.9, 10-2.3.2)
- Acidity as CaCO₃ (EPA Method M2310B).

The leaching/water extraction analysis is modified to a 2:1 liquid to solid ratio in accordance with a typical field analysis approach recommended by the State of Colorado's

Department of Minerals and Geology. The metals analysis to be run includes arsenic, cadmium, copper, lead, and zinc.

Based on the laboratory results from the water extractions, several sites may be selected that have high levels of one or more water-extractable metals. These samples are further analyzed (if the storage date has not been exceeded), or the sites are re-sampled by the methods described above. Samples are analyzed using the Toxicity Characteristic Leaching Procedure (TCLP). Metals evaluated with TCLP are arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), selenium (Se), silver (Ag), and zinc (Zn).

5 Recording and Sample Labeling

During the sampling activities a current field book is utilized to record the field conditions and sampling activities. At a minimum, the field book includes:

Date and Time:	i.e. September 21, 2001 @ 3:00pm	
Sample Location	:i.e. Outlet Waste Rock Pile – Homogeneous Unit #3 as shown on map	
Remarks:	i.e. Weather, soil color, coarseness, sample depth, tests performed and/or	to be performed,
	and other miscellaneous observations.	
Analysis:	i.e. Paste pH and conductivity	

Samples gathered are labeled with the following information:

i.e., Willow Creek Reclamation Committee
i.e. 719-658-0178
i.e. Waste Pile Characterization
i.e. Outlet Mine – Unit #3
i.e. September 21, 2001 or 09/21/01
i.e. 3:00pm or 1500
3-inches
John and Jane Doe

6 Sample Shipment

The following steps are performed to ensure proper shipment of the samples gathered as part of this SAP.

- Make sure all samples are double bagged, tightly closed, taped and labeled correctly.
- Place samples in cooler or appropriate container. Pack the empty space of each cooler with packing paper or equivalent so the samples are not tossed around during shipment.
- Fill out properly and enclose a chain of custody form, one for each cooler. Place the form in a sealed Ziploc bag within the cooler. The samples are not valid without a chain of custody form.
- Close and secure each cooler with strapping tape to prevent tampering during shipment.
- Place the proper mailing label(s) on each cooler and ship to designated laboratory for analysis.

7 Equipment

The following equipment is required to perform the sampling described in this SAP.

- Soil samples are collected in new Ziploc bags with the use of new plastic cups, bowls, and knives.
- Permanent markers, plastic bottles, and paper towels.
- pH and Conductivity Meter with electrolyte and buffer solutions for calibration.
- DI (de-ionized) water.

8 Decontamination Procedure

Prior to sampling, equipment is washed in an Alconox soap solution, rinsed in de-ionized (DI) water, and placed in a new Ziploc bag or equivalent. The procedure for making Alconox soap solution is as follows:

• Put 2 packets of Alconox in a 1 gallon jug filled about 75% full of preferably warm water and shake well – use safety goggles and nitrile gloves when washing with or making this solution.

9 Laboratory Quality Control

The laboratory will meet standard quality control protocols, including method blank and blank spike analysis, matrix spike and duplicate analyses, calibration verifications and calibration blanks. All quality control sample results shall be within acceptable criteria in order for the data to be considered accurate and precise to the degree expected by the standard test method used. All discrepancies will be reported by the laboratory.

10 Data Quality Objectives

The soil samples are being collected and analyzed to evaluate the impacts, if any, of historic mining activities on surface soils at the site, including metals-containing materials (e.g., tailings transported by water, wind, or direct placement. Additional deeper samples should be collected if different conditions are expected. Based on these data, decisions must be made regarding the need to remediate soils at the site. This will require data that are accurate and precise to the levels expected by standard test methods, complete in coverage, and representative of the soils in question. The concentrations at each location, or a statistical representation of average conditions (e.g., the 95% upper confidence limit of the mean) can then be compared to the appropriate screening or cleanup standard for the site. Generally, data that do not meet the established acceptance criteria are cause for re-sampling and re-analysis. However, in some cases, data that do not meet acceptance criteria are usable with specified limitations. Data that are indicated as usable with limitations will be clearly noted.

11 Data Reporting

The results of the sampling and analysis program will be reported to Colorado Department of Public Health and Environment (CDPHE) including a description of sampling locations and procedures, a discussion of any deviations from this SAP, a summary of the data, a location map, and a discussion of data quality. The complete laboratory analytical report, including quality control test results, will be attached.

Geochemical test procedures for field reconnaissance programs - paste pH and conductivity

Paste pH and Conductivity

Objectives

To determine the pH and conductivity of the pore water resulting from dissolution of secondary mineral phases on the surfaces of oxidized rock particles.

To indicated whether oxidation, and accumulation of contaminants in the form of secondary mineral phases, has occurred in the waste rock prior to collection of the sample.

Description of Test

Water is added to the sample to form a paste or slurry thus mobilizing secondary mineral phases and providing a medium accessible to the pH and conductivity or TDS probes. The probe is placed in the paste or slurry and the pH or conductivity value is read directly from the meter.

Equipment

- 1. pH meter equipped with a combination pH electrode.
- 2. Conductivity or TDS meter.
- 3. 50 mL beakers, or equivalent (disposable paper cups, bottom of pop can etc.)
- 4. Spatula or stirring rod (e.g. plastic coffee stirrers)
- 5. Litmus paper strips

Reagents

- 1. Standard buffer solutions, pH 4.00 and pH 7.00
- 2. Standard electrolyte solutions (for calibration of conductivity meter)
- 3. Distilled (or deionized) water

Procedure

- 1. Calibrate pH and conductivity or TDS meters using the standard solutions and following instructions provided with the meters.
- 2. Obtain approximately 25 g of fines (particles smaller than 1 mm if possible) from the rock sample to be tested, and place in a fresh or decontaminated beaker or testing container.
- 3. Add approximately 25 mL of distilled water to sample. (More water may be required if the sample is very dry or extremely fine).

Geochemical test procedures for field reconnaissance programs - paste pH and conductivity

- 4. Stir sample with fresh or cleaned spatula to form a paste or slurry. Paste should slide off spatula easily.
- 5. Tip the testing container to one side to allow a pool of water or slurry to collect in the corner. Dip each of the probes into the slurry, and allow the meter readings to stabilize. The conductivity reading should however be done first, as electrolyte from the combination pH probe may affect the conductivity of the solution.
- 6. Decontaminate probes and containers.
- 7. Record the measurements in field notebook along with a description of the rock type tested, and the general appearance of the sample.

Interpretation

High conductivity (or TDS) levels indicate there is considerable store of contaminant salts. These are usually sulphates, but can be other metal salts. When a sample is collected over depth, it is not always clear whether the stored salts are due to oxidation at that point in the sediment profile, or if the salts were generated somewhere higher in the profile and moved downwards to the sample location. Look for stains along the flow path that may indicate if this is the case.

Low pH readings indicate oxidation and acid generation has occurred, usually at the location from which the sample was collected. Readings taken on uncrushed samples in the field or lab usually provide a much better indication of the extent of oxidation than crushed samples do.

References

Sobek, A.A., Schuller, W.A. Freeman, J.R. and Smith, R.M. (1978), Field and Laboratory Methods Applicable to Overburden and Minesoils, EPA 600/2-78-054, 203 pp.

British Columbia AMD Task Force (1989), Draft Acid Rock Drainage Technical Guide, Vol I, Crown Publications, Victoria, B.C. **APPENDIX B**

SAMPLING SITE DIAGRAMS