

2000 Billings Land Reclamation Symposium

MATERIAL CHARACTERIZATION AND PRIORITIZATION OF REMEDIATION MEASURES AT THE ZORTMAN/LANDUSKY MINE SITES.

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ABSTRACT

Reclamation of the Zortman and Landusky gold mines in the Little Rocky Mountains of north-central Montana is currently being undertaken under the direction of the Montana Department of Environmental Quality and using the funds from the Reclamation Bond. As with many projects a balance must be found between the economics, technical, environmental and socio-economic issues at the sites. As part of the reclamation effort, a geochemical characterization program was developed which involved an intensive field geochemical assessment, supported by laboratory test work and 'historic' data. The objective of the characterization program was two-fold. Firstly, to identify the location, extent and probable contaminant loads from the sites; and secondly, to identify candidate materials for suitable cover and remediation purposes. Prioritization of remediation measures was then completed in an effort to assess and optimize the degree of remediation attainable with the limited financial resources available. This paper describes the material characterization program. It also describes the method and rationale developed to prioritize the remediation measures.

Additional Keywords: Zortman, Landusky, reclamation, geochemistry, remediation.

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INTRODUCTION

The Zortman and Landusky mines are located in Phillips County, Montana approximately 155 miles north of Billings (Figure 1). There has been mining in the area in one form or another since the first gold panner found a nugget in 1884. The first mill was built there in 1904 and mining continued underground off and on through to the 1970's ceasing intermittently during the two World Wars. Larger scale open pit mining and heap leach operations of the lower grade ore at Zortman and Landusky began in 1979 by Pegasus Gold Corporation and continued until 1995. Gold and silver were extracted by Carbon Absorption and Stripping and Merrill-Crowe precipitation. Both mines are currently closed and being reclaimed under the direction of the Montana DEQ using the Closure Bond Funds provided for by Pegasus under Montana Bonding requirements.

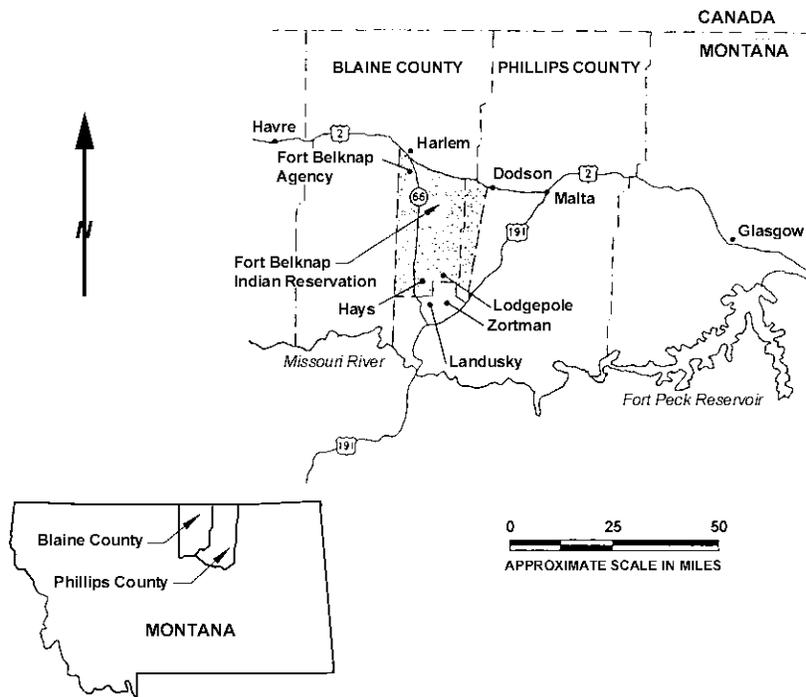


Figure 1. Location map of Zortman and Landusky Mine Sites
(after US DOI and MT DEQ, 1996)

Mine reclamation at the Zortman and Landusky mines, as with most mines, is faced with multidisciplinary issues and decisions in which compromises must be made and trade-offs evaluated. There are at least two critical issues for the Zortman/Landusky reclamation. There is (1) insufficient funding in the reclamation bond and (2) limited suitable construction material on site to complete the reclamation that was proposed in the Environmental Impact Statement (EIS) (US DOI and MT DEQ, 1996) and stipulated in the Record of Decision (ROD) (MT DEQ and US DOI, 1998) for the site. Therefore, an evaluation of the effectiveness of the specified measures and prioritization of reclamation areas and measures is being done. In order to complete this evaluation and prioritization a geochemical characterization program was undertaken.

The objective of the geochemical program was two-fold. Firstly, to identify the location, extent and probable current and future contaminant loads from the various facilities (leach pads, waste dumps and open pits) on the sites and to prioritize which areas most require a high degree of reclamation and which require less or minimal reclamation. Secondly, the program was aimed at identifying candidate materials on site for cover and remediation purposes. The characterization program was comprised of an assessment of historic information, a field reconnaissance survey and laboratory testing program. This paper presents the results of the characterization program and some discussion as to how this information will be used to prioritize remediation areas and measures.

CHARACTERIZATION PROGRAM

Historic Data

A fair amount of geochemical and geological information is available about the site, most of which was produced after 1990. In 1992, the mining company (Pegasus) filed an application for expansion of the operations. As a result, between that time and mid 1994, a number of studies were undertaken in preparation of an Environmental Impact Statement (EIS). These studies included extensive static and kinetic tests of drillcore aimed at predicting the acid generating potential of the rock mined and exposed as a result of expansion (Miller and Hertel, 1997). The mine expansion however never went forward. Therefore, the material characterized in those studies remains unmined. The vast amount of information produced in those studies is therefore of limited usefulness to the current reclamation program.

Prior to the application for expansion in the mid-1980's an extensive water monitoring program was implemented on both the Zortman and Landusky sites. As a result, a great deal of extremely valuable information has been collected on the geochemical behavior of mine elements and area, such as leach piles and mine pits. Water quality trends over time have proven very helpful in assessing the current contaminant loads from the sites and likely future water qualities. They allow trends to be established indicating the evolutionary behavior of large masses of mine disturbed materials. These results are discussed in greater detail later in the paper.

Another set of historic data that is often not fully exploited for geochemical characterization is the mined material itself. The pit walls, spent ore and waste rock materials that are currently exposed and have been for at least 5 to 10 years, since mining operations ceased, are essentially a large, 'historic' humidity cells. Simple tests such as paste pH, paste conductivity measurements and leach extraction tests on material exposed to weathering for this amount of time can provide more information than could be achieved in relatively short term laboratory tests. As a result, the field reconnaissance surveys at Zortman and Landusky were an extremely critical part of the characterization program.

Field Reconnaissance Program

The objectives of the field reconnaissance program were (1) to identify potential sources of NAG material (i.e. non-acid generating material that may be a potential source of construction and cover material) and (2) to identify and quantify potential sources of acid generating material and contaminant sources. The program consisted of paste pH and paste TDS analyses and visual identification of rock type, degree of alteration, degree of oxidation, surface precipitates and staining, presence of visible sulfides and any ‘unusual’ textures. Field logs (including photographs) were recorded and the sample locations were surveyed using a GPS system and plotted on a map.

The results of the field paste pH and paste TDS analyses are summarized in Table 1 organized by mine facility (or material type). As would be expected, samples with low pH values have higher TDS values (due to the presence of soluble minerals on the grain surfaces) and those samples with neutral pH results have low TDS values. The relationship between paste pH and paste TDS for the different material types on the Zortman and Landusky sites is shown in Figure 2. There is a clear trend whereby samples with pH values below approximately 5, show sharply increasing TDS concentrations. The samples that do not fall neatly within this trend are predominantly leach pad samples (designated by open circles on the figure) where the addition of lime and caustic soda in the leaching solutions account for moderate to high TDS values and still control the pH to circum-neutral values (i.e. the TDS results from alkalinity products not acidity/oxidation products).

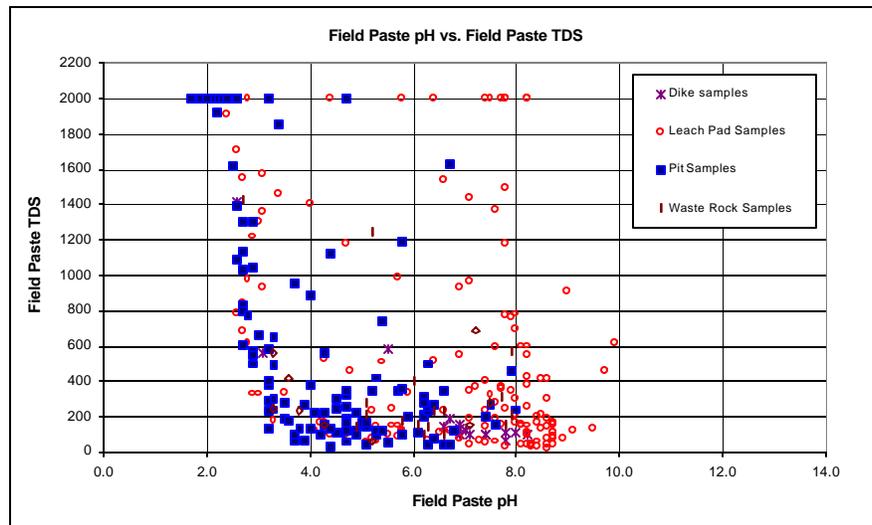


Figure 2. Paste pH versus paste TDS for Zortman and Landusky samples.

The color of the Zortman and Landusky mined material (again with the exception of the spent ore on the leach pads) is a relatively good indication of pH, or acid generating conditions. Visual inspection therefore can provide the first assessment of a material’s acid generating potential. The unoxidized porphyry materials containing fresh sulfide minerals (in particular pyrite and, on Landusky, marcasite) are typically grey in color. These materials are acid generating with pH values commonly below 3 and very high TDS concentrations. The partially oxidized porphyry material was often an olive-green to

yellow color. This color is a reflection of the presence of secondary minerals produced when sulfide minerals oxidize, such as iron oxy-hydroxides and iron sulfates. These minerals are soluble and when dissolved produce acid, therefore they are sometimes referred to as 'stored acid products'. The partially oxidized material is predominantly acid generating with pH values generally less than 4.5. The oxide porphyry material contains no visible residual sulfides and typically has paste pH values in the 4.5 to 6.0 range. This material is orangey-red in color and relatively easily differentiated from the other material types on this basis.

Table 1. Summary of mean, minimum, maximum and standard deviation values for paste pH and paste TDS results by mine facility.

ZORTMAN		MEAN	MIN	MAX	STD DEV
Leach Pad Samples	pH		1.8	9.0	2.3
	TDS	597	60	>2000	641
Pit Wall and Pit Floor Samples	pH		1.7	6.7	1.4
	TDS	758	30	>2000	786
Waste Rock Samples	pH		2.7	7.1	1.4
	TDS	316	60	1430	379
Dike samples	pH		2.6	7.4	1.6
	TDS	438	100	>2000	600
Roadcut Samples	pH		3.7	6.9	1.3
	TDS	235	70	460	192
Tailings	pH		5.8	7.6	0.7
	TDS	800	70	>2000	937
Topsoil	pH		5.0	6.8	0.7
	TDS	141	50	228	64
LANDUSKY		MEAN	MIN	MAX	STD DEV
Leach Pad Samples	pH	7.1	2.5	9.9	1.8
	TDS	602	20	>2000	678
Pit Wall and Pit Floor Samples	pH	4.2	1.9	8.0	1.9
	TDS	845	40	>2000	748
Waste Rock Samples	pH	6.2	3.3	7.9	1.6
	TDS	364	140	1250	300
Stockpile Samples	pH	7.6	6.9	8.0	0.6
	TDS	130	100	170	36
Dike Samples	pH	7.2	3.7	8.2	1.7
	TDS	117	70	190	40
Topsoil	pH	7.0	3.5	8.0	1.7
	TDS	560	90	>2000	723

Although color alone is not recommended to differentiate between material types, it is a useful classification tool for the Zortman and Landusky sites. Caution should be exercised when judging leach pad material as many surface minerals precipitating from leach pad solutions have coated the surface of much of the material and the color is a less dependent characteristic of the geochemistry. Field 'clues' including paste pH, paste TDS rock type

and color description at these sites, where the material has been exposed to weathering conditions for an extended period of time, are relatively inexpensive and very valuable pieces of information. This type of survey is often not given enough credit in similar characterization programs. The outcome of the field reconnaissance survey were large maps of each site designating potentially acid generating, moderately acid generating and non-acid generating material on the sites. These maps are continually refined as new information about the sites is obtained (e.g. results of the laboratory testing program) and will be used in the prioritization of reclamation areas.

During the reconnaissance program, samples were collected for confirmatory laboratory testing. Sampling for lab testing concentrated on obtaining representative samples with respect to rock type and geochemical type (i.e. degree of oxidation, sulfide content etc.), as well as obtaining representative samples of each mine facility (i.e. each leach pad, pit, waste dump etc.). There was a slight bias in numbers of samples collected for lab testing towards both the potential NAG materials and the ARD/metal leaching materials. The lab testing program is described in detail in the Section below.

Laboratory Testing Program

All samples collected for the laboratory testing program were submitted for paste pH and paste conductivity measurements on the as-received 'fines', modified acid base accounting (ABA) tests, inorganic carbon and leach extraction analyses. Subsets of these samples were also analyzed via forward acid titration, multi-element ICP, net acid generation (NAG) tests and sieve analyses. Some of the more critical results from these tests are discussed in the following sub-sections.

Paste pH and Paste Conductivity Results

Paste pH and paste conductivity tests on the as-received 'fines' were completed for two reasons. Firstly as a quality control/quality assurance check on the paste pH and paste TDS values obtained in the field using the hand held field instruments. The paste pH and paste conductivity measurements in the lab were taken on the as received 'fines' using a 1:1 solids to distilled water ratio to mimic as close to possible the methodology used in the field. Secondly, it is believed to be a more representative result than the paste pH and paste conductivity values on the same sample prepared for Acid Base Accounting (ABA) tests, i.e. the crushed samples. In effect, this crushing liberates the alkalinity from the matrix of a sample thereby effecting the paste pH. Figure 3 is provided to show the relationship between the field and lab paste pH measurements on the as-received fines (or un-crushed samples) as compared to the field and lab paste pH measurements on the crushed split sample for ABA testing. This graph clearly shows that crushing the samples liberates more alkalinity (and therefore results in higher pH values) than is available in the field. The results serve as a caution that one cannot rely on paste pH values obtained on a crushed sample as indicative of field conditions. Measurements of field paste pH should always be done on the uncrushed fines, this an important consideration when selecting a drilling method for sample recovery in waste rock and leach piles.

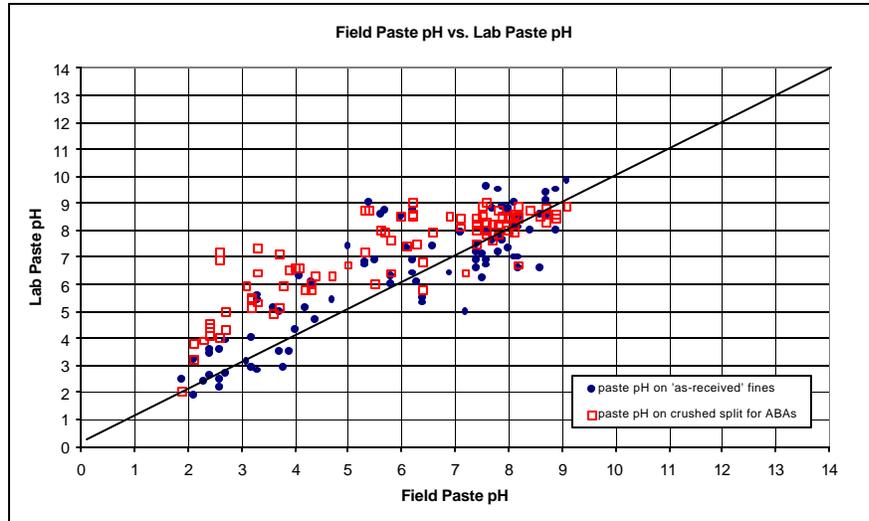


Figure 3. Field paste pH versus lab paste pH on un-crushed and crushed samples.

Modified Acid Base Accounting (ABA) and Inorganic Carbon Results

The modified ABA test is used to determine the balance between the acid producing (sulfides) and acid consuming components of a sample. The results of this test for the Zortman and Landusky samples are provided in summary form in Table 2 by material type.

A very definite trend can be seen in the samples (except for the leach pad material) with respect to the total percent sulfur and field paste pH (Figure 4). Almost all samples (excluding leach pad samples) with total sulfur contents greater than 0.2% have field paste pH values less than 5.0. This percentage of sulfur is far less than would be visible in the field. This suggests that there is very little neutralization or buffering capacity in the material except for that added to the leach pad material. It can be expected that once the alkalinity in the leach pad samples is exhausted that these samples will also plot within the dotted lines outlining the apparent natural trend of the other materials on site.

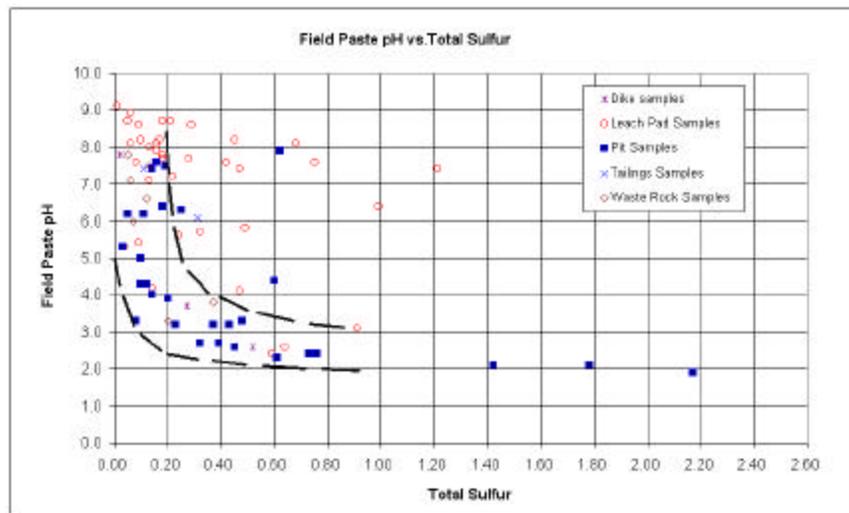


Figure 4. Field paste pH versus Percent Total Sulfur.

Table 2. Summary of modified ABA and inorganic carbon results by material type

LOCATION DESCRIPTION		PASTE pH	S(T) %	S(SO4) %	AP	NP	NET NP	NP/AP	TIC %
ZORTMAN									
Leach Pads	MIN	4.1	0.1	0.0	0.0	-1.4	-25.5	0.2	0.0
	MAX	8.7	1.0	0.4	25.6	12.1	10.8	9.7	0.1
	MEAN		0.3	0.1	6.2	3.6	-2.6	1.7	0.0
	STD DEV		0.3	0.1	6.5	2.9	7.8	2.2	0.0
Pit Wall and Pit Floor Samples	MIN	2.0	0.0	0.0	-1.3	-27.7	-59.6	0.2	0.0
	MAX	9.2	2.2	1.1	49.4	19.6	17.1	7.9	0.2
	MEAN		0.5	0.2	10.4	1.8	-8.6	2.0	0.1
	STD DEV		0.7	0.3	14.3	11.2	21.3	2.2	0.1
Roadcut & Waste Rock Samples	MIN	4.9	0.2	0.2	-1.6	-0.2	0.9	0.2	0.0
	MAX	6.3	0.3	0.3	2.8	3.7	1.3	1.3	0.0
	MEAN		0.3	0.2	0.6	1.7	1.1	0.7	0.0
	STD DEV		0.1	0.0	3.1	2.8	0.3	0.8	-
LANDUSKY									
Leach Pads	MIN	5.9	0.0	0.0	-0.9	-0.8	-26.4	0.1	0.0
	MAX	8.9	1.2	0.3	27.2	15.6	12.8	5.6	0.2
	MEAN		0.4	0.1	8.3	4.1	-4.2	1.6	0.0
	STD DEV		0.4	0.1	9.6	3.6	11.1	1.9	0.0
Pit Wall and Pit Floor Samples	MIN	3.2	0.1	0.0	0.0	-5.4	-36.3	0.2	0.0
	MAX	9.0	1.6	0.5	50.0	389.4	387.8	249.2	5.0
	MEAN		0.6	0.2	12.9	47.5	34.6	23.2	1.0
	STD DEV		0.5	0.1	14.4	99.7	95.4	71.2	1.5
Waste Rock Material	MIN	5.9	0.1	0.0	0.3	0.2	-8.9	0.4	0.0
	MAX	8.7	0.4	0.2	9.1	215.8	215.4	690.4	2.5
	MEAN		0.2	0.1	3.1	94.5	91.5	212.8	1.4
	STD DEV		0.1	0.1	3.5	97.4	99.7	323.7	1.1

Figure 5 is a plot of neutralization potential (NP) versus acid potential (AP) in kg CaCO₃/tonnes equivalent. This type of graph is typically used to report results of ABA testing. In general, the samples that plot above the 1:1 line (~60%) would be considered potentially acid generating, those that plot below the 3:1 line (~28%) would be considered non-acid generating and those that fall between the two lines (~12%) would be classified as 'uncertain' with respect to acid generating potential. It takes very little sulfur content in a sample for that sample to plot below the NP/AP ratio of 1:1, this again suggests that there is very little neutralization potential in the samples to 'balance' the acid generating potential imparted by less than a quarter of a percent sulfur.

Forward Acid Titration Results

The forward acid titration test is done to determine, qualitatively, the acid neutralizing capacity of a sample by adding measured amounts of acid to the sample to lower the pH. The amount of acid required to reach each pH interval is dependent on the amount of

neutralizing material available. As the pH decreases, different minerals react to neutralize (or buffer) the added acid. Within the pH range of 5.5 to 7.0 carbonate minerals in the sample dissolve and neutralize the acidity. If there are significant carbonates present a 'step' or flattening out of the curve will occur within that pH range (i.e. 5.5 to 7.0). A few of the results are shown below in Figure 6. The leach pad sample is the only sample showing any degree of flattening in this range. This is likely a result of the added alkalinity in the leach pad solutions. Between the pH range of 3.0 to 3.7, limonite (FeOOH) will buffer acid. This may be occurring to some degree in these samples. At even lower pH values (i.e. below ~3), aluminosilicate minerals such as the feldspars in the samples will dissolve and buffer added acid. This is likely the reason that these results show a long flattening tail below pH of 2.0.

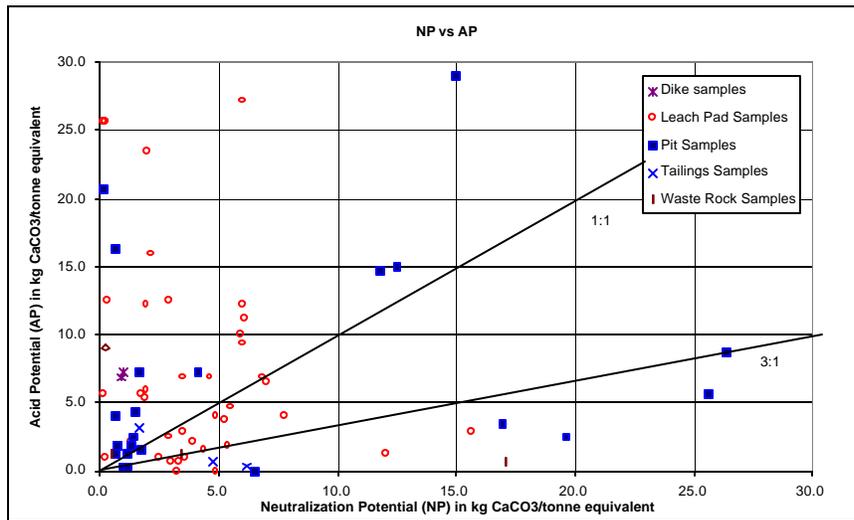


Figure 5. Neutralization Potential (NP) versus Acid Generating Potential (AP).

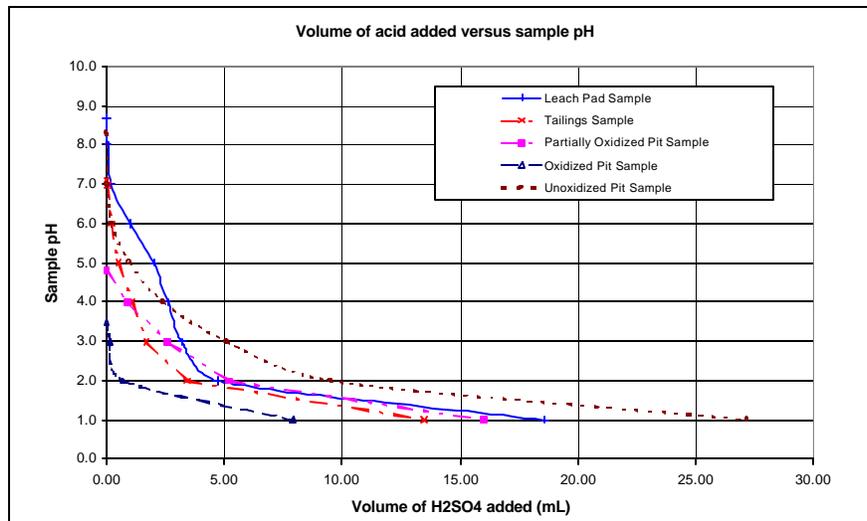


Figure 6. Forward Acid Titration Results.

Net Acid Generation (NAG) Results

The net acid generation test was used to determine the net acid remaining, if any, after complete oxidation of the materials with a strong oxidant (hydrogen peroxide) and allowing complete reaction of the acid formed with the neutralizing components of the material. The NAG test provides a direct assessment of the potential for a material to produce acid after a period of exposure and weathering and is used to refine the results of the ABA predictions. One of the great advantages of the NAG test is that it allows an assessment of the kinetics of the reactions in a sample in a relatively short period of time.

Some of the samples collected were analyzed using the NAG method with an industrial H_2O_2 reagent at a starting pH of 5.5. The experiments were run for approximately 3 days and the pH, Eh and temperatures were recorded at intervals throughout that period. The results of pH are plotted in Figure 7. The following classification criteria (Lapakko and Lauwrence, 1993) were used to assess the acid generating potential of those samples tested with the NAG method.

Final $NAG_{pH} > 5.5$	Non-acid generating
Final NAG_{pH} between 3.5 and 5.5	Uncertain to low risk acid generating potential
Final $NAG_{pH} < 3.5$	High risk of acid generating potential

Therefore, based on these results, two of the samples tested (Tailings and Unoxidized Pit Samples) would be considered non acid generating (Final $NAG_{pH} > 5$), one sample (Leach Pad Sample) would be classified as ‘uncertain’ (Final NAG_{pH} between 3 and 5) and two samples (Unoxidized and Partially Oxidized Pit Samples) would be considered acid generating (Final $NAG_{pH} < 3$). After approximately 300 minutes (5 hours) the samples are at or very near their Final NAG_{pH} . The uncertain sample is “marginal” and results appear to indicate two clearly different and definable behaviors. The first three are non-acid generating (with little buffering capacity) and the latter two are clearly acid generating.

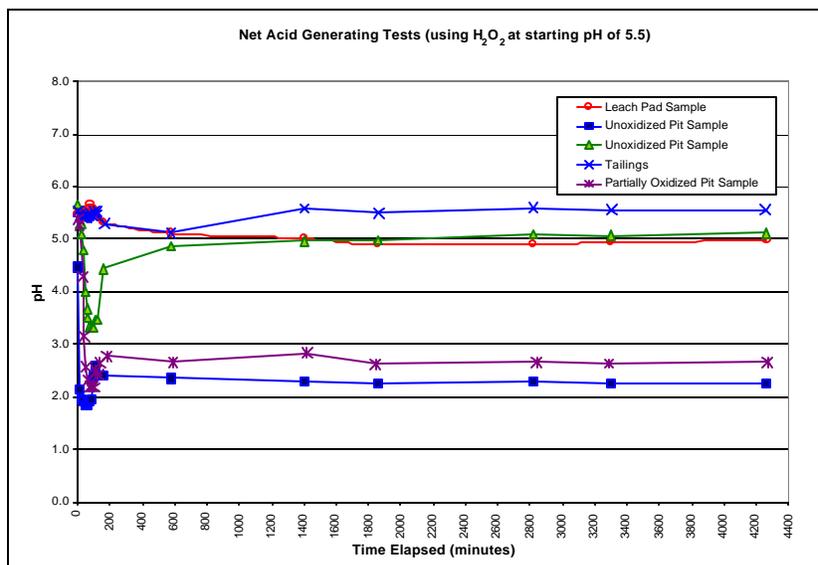


Figure 7. Net Acid Generation Tests – pH versus Time for Selected Samples.

Leach Extraction Tests

Leach extraction tests were completed in order to characterize and quantify the soluble contaminant content of a sample. The procedure used for these analyses was the EPA 1312 leach extraction test using a leachate reagent of de-ionized water acidified to a pH of 5.0 to 5.5 to represent rainwater. The procedure uses a solid to liquid ratio of 1:2. The leachate concentrations are representative of current ARD evolution state and the quantity of leach water compared with solid sample. Field conditions have much higher solid:liquid ratios and ARD conditions will mature with time. The resultant leachate concentrations therefore are not necessarily representative of what concentrations would be expected in the field. An assessment of the current field water qualities from material exposed on the surface was completed by accounting for the ‘dilution’ factor inherent in the leach extraction test and assuming a field moisture content of ~10% (as opposed to a moisture content of 200% used in the test). In other words, the leachate concentrations were multiplied by a factor of $[10/(200+10)]$. These calculated concentrations however do not yet represent field water qualities. During the leach extraction tests, the dilution of solute concentrations in the leachate can cause the dissolution of secondary mineral phases that were previously in a solid phase (i.e. oversaturated). It was therefore necessary to “re-instate” the solubility controls on the solute concentrations by modeling the calculated leachate concentrations using the geochemical equilibrium model MINTEQA2 (Allison et al., 1991). Water quality predictions were then made for the surface water runoff from the various material types. Table 3 provides the predicted water qualities from those areas considered highly acid generating, moderately acid generating and non-acid generating for both the Zortman and Landusky sites.

Table 3. Predicted water quality of material with various degrees of acid generating potential on both Zortman and Landusky.

Parameter (mg/L)	Predicted Water Quality of:					
	Highly acid generating material		Moderately acid generating material		Non acid generating material	
	ZORTMAN	LANDUSKY	ZORTMAN	LANDUSKY	ZORTMAN	LANDUSKY
pH	< 3]	< 3]	[3 - 5]	[3 - 5]	> 5]	> 5]
Al	161	925	59	87	0	0
As	1.34	6.01	0.00	0.00	0.00	0.00
Ca	40	85	154	146	10	218
Cd	0.00	0.10	0.15	0.10	0.00	0.00
CO ₃	0	0	8	0	26	17
Cr	4.90	0.47	0.37	0.15	0.00	0.00
Cu	1.62	1.18	0.71	0.00	0.10	0.30
Fe	0.24	2.37	0.00	0.05	0.00	0.00
K	0.0	0.0	305.0	0.0	0.0	78.7
Li	22.35	27.46	10.45	0.00	0.00	0.00
Mg	55	364	689	380	14	166
Mn	2	33	40	11	0	8
Ni	0.43	1.59	1.53	0.68	0.00	0.00
Pb	0.00	0.00	0.02	0.00	0.00	0.00
Si	0.12	0.03	0.53	0.70	0.85	0.30
SO ₄	3988	3245	394	494	11	148
Zn	0.77	15.48	0.72	4.66	0.06	0.23

WATER QUALITY MONITORING DATA

As mentioned above, a relatively extensive groundwater and surface water monitoring program was started at the site in the mid-1980's. Water quality trends over time have allowed us to predict apparent 'mature' water qualities. Sulfate concentrations and pH trends over time for two wells believed to be representative of the 'mature' water qualities as a result of acid generation and contaminant release on the both Zortman and Landusky are provided in Figures 8 and 9 respectively. It appears that the 'terminal' pH for ARD impacted waters on Zortman is approximately 0.5 of a pH unit lower than that on Landusky and the sulfate concentrations are also higher on Zortman (perhaps by a factor of 2).

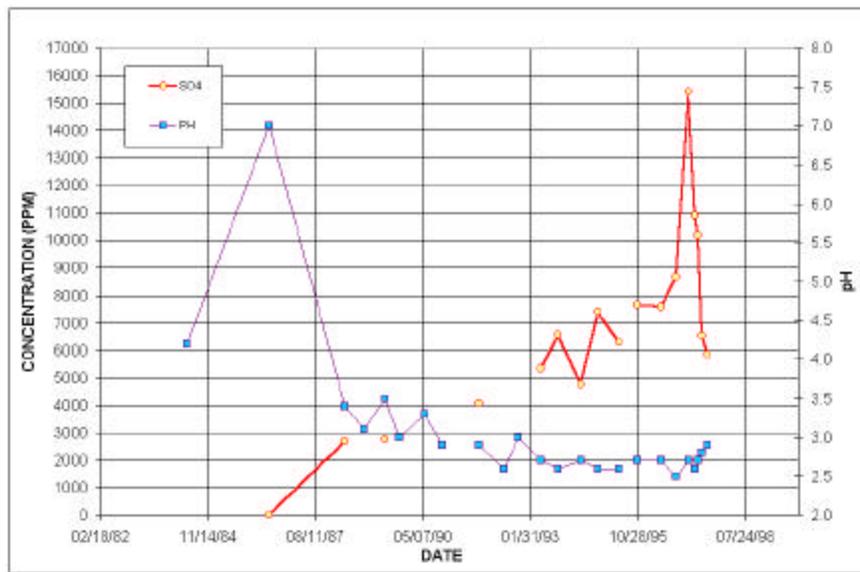


Figure 8. SO₄ conc. and pH over time at a groundwater monitoring well on Zortman.

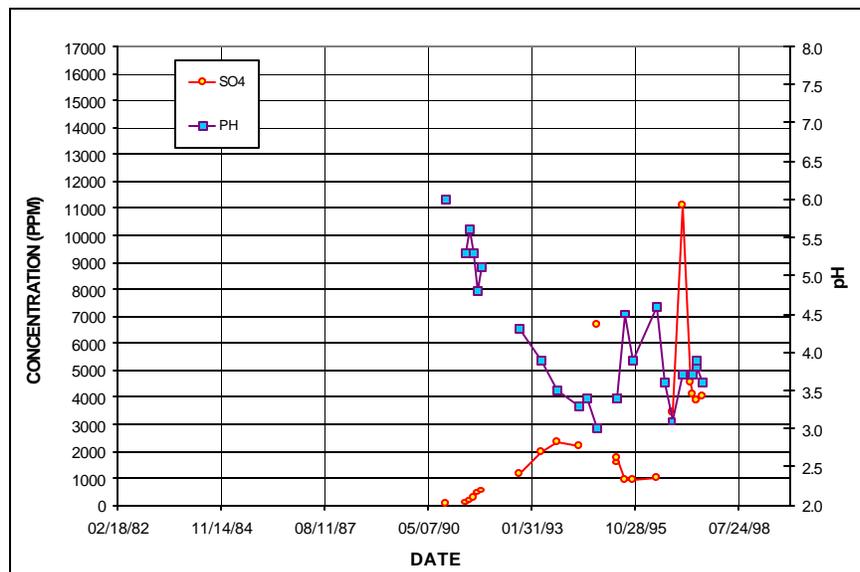


Figure 9. SO₄ conc. and pH over time at a groundwater monitoring well on Landusky.

PRIORITIZATION OF REMEDIATION AREAS AND MEASURES

The field reconnaissance results, laboratory test results, predicted surface water qualities and the data obtained from the surface and groundwater monitoring program at the sites, together with the site water balances are being used to develop current and likely future mass balance and contaminant load estimations for the sites. These estimations along with the engineering volume mass balance and material costing will be incorporated into a Multiple Accounts Analysis, or MAA, (Robertson and Shaw, 1998) decision-making tool for the prioritization and evaluation of the likely results of certain reclamation areas and measures. The MAA evaluation of the various reclamation alternatives is currently underway as a cooperative effort between ourselves, the Montana Department of Environmental Quality, the U.S. Bureau of Land Management, U.S. Environmental Protection Agency and the Fort Belknap Tribal Council. Past experience with this type of decision making has proven extremely successful for multi disciplinary projects involving multiple stakeholders such as with the Zortman and Landusky Reclamation Project.

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Amelioration of Sodic Spoils by Weathering in the Powder River Basin, Montana

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ABSTRACT

The coal-bearing formations in the Western United States locally contain sodic materials that have traditionally been considered unsuitable as reclamation substrates. Significant regulatory and operational resources are directed toward the avoidance of sodic materials for reclamation under the assumption that they are toxic. However, a comprehensive assessment of the physicochemical factors affecting sodium toxicity and sodicity related permeability reductions indicate that many sodic spoils are conditionally acceptable as reclamation substrates from a short-term perspective. The acceptability of these spoils is predicated on the time-transgressive reduction in sodicity associated with leaching and primary mineral weathering. Thus, the rate and trajectory of weathering in the spoils is important for determining their suitability as soil substitutes over the long-term. We will present new data from reclaimed sodic spoil test plots established at the Decker Coal Mine in the late-1970's that demonstrates the weathering related amelioration of spoil sodicity. Specifically, decreases in the spoil pH and sodium adsorption ratio (SAR) were accompanied by increases in salinity. The spoil solution chemistry is interpreted to indicate a shift from carbonate-dominated to sulfate-dominated systems. Data from the cover soils confirms that convective leaching and the relatively rapid decrease in spoil sodicity eliminates concerns associated with cover soil sodification by diffusional processes.

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EVALUATION OF FERRIC OXIDE FOR ADSORPTION OF ARSENIC LEACHING FROM A MINE WASTE REPOSITORY

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ABSTRACT

Modeling of leachate production through a proposed mine waste repository along Silver Bow Creek near Butte, Montana showed that arsenic levels exceeded the State of Montana standard (WQB-7) of 18 µg/L. Therefore, an investigation was conducted with ferric oxide to determine its potential in attenuating arsenic from leachate produced in an acidic-metalliferous tailings repository. Acidic-metalliferous tailings were neutralized with lime and placed in columns overlying no ferric oxide (no-treatment), ferric oxide thickness at 1.67 percent of the tailings thickness, and ferric oxide thickness at 3.33 percent of the tailings thickness. These columns produced leachates containing mean As concentrations of 323, 192, and 156 µg/L respectively. The 1.67 and 3.33 percent ferric oxide treatments reduced corresponding mean As concentrations by 41 and 52 percent. The ferric oxide layers also adsorbed large amounts of copper and zinc, significantly reducing concentrations of these metals in leachate.

Acidic-metalliferous tailings neutralized with lime were also placed in columns atop a 7.62 cm and a 15.24 cm thick layer of ferric oxide. The As concentrations in leachates were reduced 68 percent and 79 percent compared to the control, respectively.

These results indicate that when leachate As levels were in the range of 162-324 µg/L, the ferric oxide layers tested did not adsorb sufficient As to reduce the concentration to below the Montana standard (WQB-7). Using a regression model, it was estimated that the ferric oxide layer would need to be 25.4 cm thick, to remove sufficient As to meet the WQB-7 standard.

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INTRODUCTION

The Streamside Tailings Operable Unit extends for a distance of 42 km along Silver Bow Creek from west of Butte, Montana to the Warm Springs Ponds (Figure 1). The operable unit contains more than 70,000 m³ of flood plain and channel sediments, and railroad beds which contain high levels of arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) from mining and smelting wastes (MDEQ and USEPA 1995). As part of the remedial design for the unit, tailings impacted soils which cannot be safely treated in place will be excavated along with channel sediments and railroad beds, and placed in Mine Waste Relocation Repositories (MWRR) located outside the 100 year flood plain boundary (MDEQ and USEPA, 1995). Compliance with Applicable or Relevant and Appropriate Requirements (ARARs) requires consideration of the migration of contaminants to ground water in that, (1) leachates from the MWRR must not exceed the Montana Department of Environmental Quality (MDEQ) WQB-7 standards for ground water (MDEQ, 1995), and (2) the leachate must not degrade the ground water quality. Excavated waste materials placed into the MWRRs will be limed to minimize the leaching of metals and subsequent migration of these metals to ground water.

Numerous MWRR designs were evaluated for potential leachate production by Maxim (1998). Leachate production calculated with the HELP model ranged from 0.02 cm to 5.54 cm per year for these scenarios. One alternative, (45.7 cm of cover soil over neutralized wastes at a near stream location), had a leachate production of 1.55 +/- 1.52 cm per year and was selected for the preliminary final design for reclamation of a portion of the Streamside Tailings Operable Unit.

The potential for leachate production from a MWRR raised the concern that contaminants, especially arsenic, may migrate to ground water. Therefore, Maxim (1998) evaluated the ability of arsenic to leach from lime amended wastes from the operable unit. They found that unamended wastes yielded leachate with 350 µg/L As, while lime amended wastes yielded 210 µg/L As. Both of these leachates exceeded the WQB-7 standard for As of 18 µg/L. However, continued bench top tests indicated that the geologic materials beneath the proposed MWRR location would attenuate As further to levels of 18 to 20 µg/L from an initial

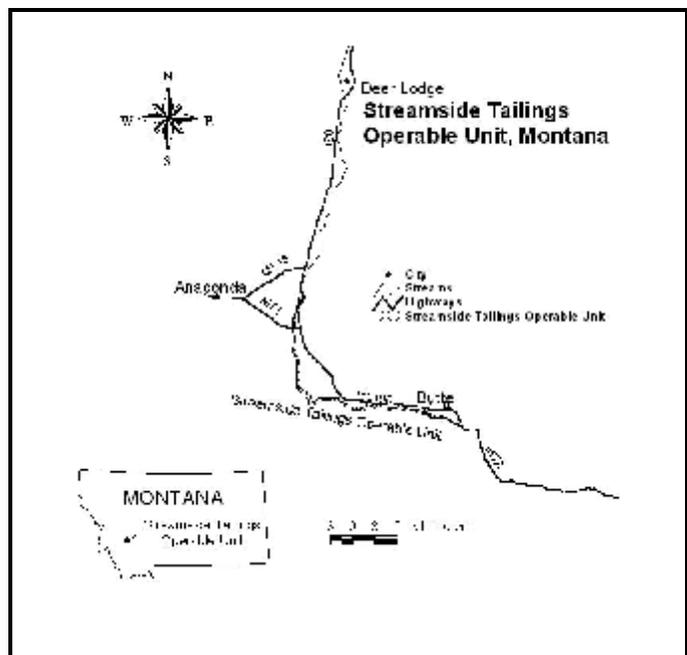


Figure 1. Streamside Tailings Operable Unit along Silver Bow Creek, near Butte, Montana.

concentration of 200 µg/L.

The solubility of As has been shown to be strongly controlled by adsorption onto iron oxide surfaces (Klaus et. al., 1998). For example, Woolson et al. (1971) concluded the presence of iron (Fe) in soils is the most effective factor in controlling the mobility of arsenate. The solubility product for arsenate combined with iron is 100-fold less than when combined with calcium associated with soil-clay systems.

The intent of this bench scale study was to determine if the utilization of iron oxide materials at the base of a MWRR can increase adsorption of As from leachate and hence, prevent or notably reduce potential arsenic loading to ground water.

STUDY OBJECTIVES

This investigation served to evaluate the feasibility of constructing an adsorption layer beneath the mine waste to decrease arsenic release from a MWRR. One adsorption material, ferric oxide (Fe₂O₃) having the common mineral name hematite, was tested. The material used was a commercial “natural red iron oxide” of minus 60 mesh particle size (≤ 0.25 cm). Hematite is the most widely utilized iron ore mined in the United States and is the primary iron mineral in taconite which averages about 25 percent iron (Mason and Berry, 1968). Objectives of this investigation were to:

- determine the degree to which As in leachate at 200 µg/L can be adsorbed by ferric oxide; and
- evaluate the quantity of ferric oxide required in a mine waste repository to reduce As in leachates to levels that meet State ground water quality standards.

METHODS

This investigation was divided into two phases: Phase I tested the adsorption characteristics of ferric oxide alone using a synthetic arsenic solution; and Phase II simulated repository field conditions by placing ferric oxide at the bottoms of columns loaded with amended mine waste. Phase I methods and results will not be presented in this paper, but are available in Dollhopf et. al. (1999).

Ferric oxide material (natural red iron oxide) was obtained from Dyce Chemical/HCl in Billings, Montana. The material was ≤ 0.25 mm in particle size, and was analyzed for total Al, As, Cd, Cu, Fe, Mn, Pb, Si and Zn by XRF (Table 1). The capacity of this material to adsorb a synthetic arsenic leaching solution was examined in Phase I, and was found to reduce solutions containing 115.2 to 108.0 µg/L As to levels less than 18 µg/L (Dollhopf et. al., 1999).

Bulk tailings samples were collected from test pit locations SC-1014 (38-48 cm depth) and 1N-1088 (0-40.6 cm depth) within the Streamside Tailings Operable Unit in an attempt to duplicate the tailings samples which Maxim (1998) used in their earlier leachate tests. The tailings samples were air dried, sieved to ≤ 2 mm, and mixed together in the proportion of approximately 24 percent 1N-1088 and 76 percent SC-1014 to maximize arsenic content. Subsamples of the tailings were analyzed for the items listed in Table 1.

Table 1. Analytical testing methods for the Streamside tailings bulk samples.

Parameter	Constituents	Method
Preparation and Rock Content	Volumetric rock content	ASTM D421-85 and ASTM D422-63 (ASTM, 1997)
Particle Size, Soil Textural Class	Dry Sieve Analysis, weight and volumetric basis	ASTM D422-63 (ASTM, 1997), Modified Day Method 15-5 (ASA, 1986)
Percent Moisture	Gravimetric	ASA Method 21-2.2.2 (ASA, 1986)
Saturation Percent	Saturation Percent	ASA Method 21-2.2.2 (ASA, 1986)
Electrical Conductivity	Saturated Paste Extract	USDA Handbook 60, Method 3a, 4b (U.S. Salinity Lab Staff, 1954)
pH	Saturated Paste Extract	USDA Handbook 60, Method 3a, 21c (U.S. Salinity Lab Staff, 1954)
Total Lime Requirement	Modified Sobek Acid Base Account/ SMP Active Acidity	Modified Sobek-Sulfur Fractionation SMP Single Buffer (Sobek et.al., 1978)
Total As and Metals	As, Cd, Cu, Pb, and Zn	by XRF Ashe (1995)

Lime kiln dust (LKD) was collected from the same source (Continental Lime Co., Townsend, MT) that Maxim (1998) used in their study to amend the tailings. The LKD was sieved to ≤ 0.25 mm and analyzed for percent moisture (Method 21-2.2.2; ASA, 1986) and calcium carbonate equivalence (CCE) (ASTM C25-96a, ASTM, 1997). Equation 1 was used to calculate the lime application rate for the mixed tailings sample. The calculated rate was adjusted to account for the calcium carbonate equivalence (lime as CaCO_3) and percent moisture of the LKD.

$$\text{LR} = [31.25 (\text{HNO}_3\text{-S} + \text{Residual-S}) + 23.44 (\text{HCl-S}) + \text{SMP}] 1.25 \quad [1]$$

where:

LR = Lime requirement (tons CaCO_3 /1000 tons),
 $\text{HNO}_3\text{-S}$ = Nitric acid soluble sulfur (%),
 Residual-S = Sulfur (%) left after acid extractions,
 HCl-S = Hydrochloric acid soluble sulfur (%),

SMP = SMP single buffer lime rate (tons CaCO₃ /1000 tons), and
 1.25 = A mixing design factor to adjust for field incorporation.

Nine modified (no ceramic plates) Tempe cells were set up using 45.7 cm high and 8.2 cm diameter polycarbonate cylinders. Each column base was retained, in a downward sequence, with a number 42 Whatman filter, a fine nylon mesh with 0.0036 cm openings, and a fine (0.0127 cm openings) 304 stainless steel screen. *Treatment 1* (control) consisted of 2322 g of LKD amended tailings. *Treatment 2* consisted of 2322 g of LKD amended tailings overlying 59.26 g (1.67 % of tailings thickness) of ferric oxide. *Treatment 3* consisted of 2322 g of LKD amended tailings overlying 118.46 g (3.33 % of tailings thickness) of ferric oxide. The ferric oxide thicknesses correspond to a 7.6 cm and 15.2 cm adsorptive layer beneath a 4.6 m high MWRR. Each of the treatments was replicated three times. A second nylon screen was placed on the upper soil surface of all columns to dissipate energy from water additions and therefore prevent erosion of the surface.

Deionized water was used to leach the columns and was pushed through the material under an air pressure of 50 kPa (0.5 bars). Leachate was collected in 82 ml aliquots representing each 1.5 cm of applied water. The 1.5 cm of water represents Maxim's (1998) prediction of potential yearly leachate production based on the chosen MWRR design. A total of 4182 ml was leached from each column. The extraction time for each aliquot averaged approximately 30 minutes. The pH and electrical conductivity of each 82 ml aliquot was determined in the laboratory. The aliquot representing year one was also analyzed for total As, Cd, Cu, Pb, Mn, and Zn (Table 2). Aliquots for years 5 and 10 were analyzed for total As. The aliquot for year 50 was analyzed for total As, and dissolved As, Cd, Ca, Cu, Fe, Pb, Mg, Mn, Na, Zn, hardness and sodium adsorption ratio (Table 2).

Table 2. Tempe cell and column leachate analytical parameters.

Parameter	Analysis Method
pH	150.1 (USEPA 1979)
EC	120.1 (USEPA 1979)
As (V), As (III), As (total), Ca, Cd, Cu, Fe, Mg, Mn, Na, Pb, Zn	EPA CLP SOW 788 (USEPA 1988)

After 4182 ml of leachate was attained from each column, more ferric oxide was added to one of the *Treatment 2* columns to equal 815.67 g (7.62 cm, 22.9% of waste thickness). Furthermore, 1631.34 g (15.24 cm, 45.8 % of waste thickness) of ferric oxide was added to the bottom of one of the *Treatment 1* (no ferric oxide) columns. The two modified columns and a *Treatment 1* column were brought to saturation, and 82 ml of leachate was produced. The leachates were analyzed for dissolved As to determine if further As could be removed from the leachate with even thicker amounts of ferric oxide.

RESULTS

Ferric Oxide and Tailings

The chemical constituents of the ferric oxide material are shown in Table 3. The ferric oxide product contained approximately 77.2 percent Fe_2O_3 in combination with oxides of silica, aluminum, calcium and magnesium as well as other impurities. The oxides of Ca and Mg may serve to provide alkalinity into a leaching solution. Impurities included 55.4 to 66.6 mg/kg total As and 3250 to 3310 mg/kg total Mn. Total levels of Zn, Cu, Cd, and Pb were relatively low.

Table 3. Manufacturer's analysis and total elemental concentrations found in two samples of ferric oxide analyzed by XRF.

Constituent	Dyce Chemical/HCL Label Information	Sample A SSTAASSFE1	Sample B SSTAASFE2
Aluminum (%)	not available	1.44	1.78
Arsenic (mg/kg)	not available	66.6	55.4
Cadmium (mg/kg)	not available	none detected	none detected
CaO (%)	0.5	not available	not available
Copper (mg/kg)	not available	149	139
Iron (%)	54.0	55.0	56.5
Fe_2O_3 (%)	77.2	not available	not available
Manganese (mg/kg)	not available	3310	3250
MgO (%)	1.1	not available	not available
Lead (mg/kg)	not available	none detected	none detected
Zinc (mg/kg)	not available	67.2	72.8
Silica (%)	not available	10.78	11.65

The results of the tailings analyses are shown in Tables 4 and 5. Based on these results, the tailings have slightly lower total As levels than those used in the Maxim study (1998). However, other metals such as Cu and Zn are much higher. According to the analysis of the sulfur fractions and equation [1], 12.5 tons CaCO_3 /1000 tons of tailings was required to neutralize the active and potential acidity. The rate was adjusted to 15 tons LKD/1000 tons to account for moisture content and calcium carbonate equivalence of the LKD.

Table 4. Physiochemical characteristics of tailings samples.

Sample	Texture	Moisture	Saturation	pH	Electrical conductivity	As	Cd	Cu	Pb	Zn	Comments
	USDA	% Mass	% Mass	su	dS/m	mg/kg					
Maxim study (1998)	Sandy Loam	NA	NA	4.5	NA	1059	22	1717	2243	3337	tailings composite
SSTAASTLS4	Sandy Loam	2.79	36.99	6.00	2.80	879	11.2	3500	4070	6350	Composited Bulk Sample 24/76 mix
SSTAASTLS5	Sandy Loam	2.81	38.77	6.06	2.81	859	10.4	3430	4070	6200	Composited Bulk Sample 24/76 mix

Table 5. Sulfur fractionation and CaCO₃ requirements for the tailings bulk sample.

Sample	Neut. Potential	Acid Potential	Acid/Base Potential	Non Sulfate Sulfur	Total Sulfur	H ₂ O Extractable Sulfur	HCl Extractable Sulfur	HNO ₃ Extractable Sulfur	Residual Sulfur	SMP Buffer Lime Requirement
	tons CaCO ₃ /1000 tons			%						tons CaCO ₃ /1000 tons
Maxim (1998)	1.7	16	-15	NA	1.16	0.7	0.2	<0.1	0.4	13
SSTAASTLS-4	5	8	-3	0.26	0.63	0.37	0.06	0.14	0.06	2.4
SSTAASTLS-5	6	10	-4	0.31	0.60	0.29	0.11	0.15	0.05	1.10

Leachate Chemistry

Arsenic concentrations in leachate from the two ferric oxide treatments were, with the exception of year 10, consistently lower than leachate concentrations from the no-treatment columns (Table 6). A statistical comparison for each data set (years 1, 5, 10, and 50) indicated that the ferric oxide treatments were significantly different for year one from the untreated column As concentrations. Five and 50 year treated column As concentrations were significantly different from the no-treatment sample concentrations, and no significant differences were found for year 10 (Table 6). The latter finding is due in part to the large variation in concentrations from the no-treatment columns which produced a large standard deviation (157 $\mu\text{g/L}$) for these samples. The means of all leachate samples from the no-treatment, 1.67 percent ferric oxide, and 3.33 percent ferric oxide were 323, 192, and 156 $\mu\text{g/L}$ total As respectively. The addition of further ferric oxide to two of the columns further reduced arsenic levels, but not below the target of 18 $\mu\text{g/L}$ (Table 7). Leachate As concentrations suggest the ferric oxide material has a capacity to attenuate As.

In addition to arsenic, the metals Cd, Cu, Pb, Mn, and Zn were determined for year one and year 50 samples (Table 6). Cadmium values were at or below the laboratory detection level of 5 $\mu\text{g/L}$ for all leachate samples. Copper values in leachate from the ferric oxide treatments were 73-75 percent lower than those in the no-treatment. Manganese levels were lower in the treated cell leachates for year 1, but all levels (treated and no-treatment) were high in year 50 leachates.

Ferric Oxide Thickness

The ferric oxide thicknesses used in the study reduced arsenic values in leachate solution, but not to the WQB-7 standard of 18 $\mu\text{g/L}$. A linear regression of the log transform of concentrations (\log_{10}) versus ferric oxide thickness suggests approximately 25.4 cm of ferric oxide would be required to meet the WQB-7 standard of 18 $\mu\text{g/L}$ with an R^2 of 0.94 (Figure 2). However, the log base curve fit may not accurately represent these data when arsenic values fall below those used to predict the model. Arsenic adsorption data were also compared with Freundlich and Langmuir type adsorption curves. The arsenic data fit the Langmuir model well ($R^2 = 0.99$) and show that with increasing arsenic concentrations in equilibrium, more arsenic is adsorbed (Figure 3). However, the model has a negative slope which yields a negative adsorption maximum.

CONCLUSIONS

Ferric oxide at 1.67 percent and 3.33 percent of tailings thicknesses reduced mean arsenic levels in leachate by 41 and 52 percent compared to leachate from amended tailings and no ferric oxide layer. These results show that ferric oxide is capable of removing significant

amounts of arsenic from solution. However, the ferric oxide treated leachates still had mean arsenic levels at 192 µg/L and 156 µg/L which is above the WQB-7 standard of 18 µg/L As. The use of thicker amounts of ferric oxide (22.9% and 45.8 %) reduced arsenic values further, but not at or below the WQB-7 standard. A log regression model suggests that a ferric oxide layer at least 25.4 cm thick is required to reduce arsenic levels to 18 µg/L in leachate emanating from the columns tested.

Constituent	Leachate Year	Treatment		
		1 No Ferric Oxide	2 1.67 % Ferric Oxide Thickness	3 3.33 % Ferric Oxide Thickness
As (µg/L)	1	283.3a	136.33b	99.67c
	5	300.67a	169.67b	152.33b
	10	508.0a	377.33a	286.0a
	50	202.0 (235.33)a	82.67 (99.00)b	109.33 (125.67)b
Cd (µg/L)	1	3.33a	< 5a	< 5a
	50	(< 5)a	(< 5)a	(< 5)a
Cu (µg/L)	1	400.67a	102.67b	116.33b
	50	(554.67)a	(108.00)b	(108.67)b
Mn (µg/L)	1	797a	42.67b	16.67c
	50	(3006.67)a	(2615.00)a	(5953.33)a
Pb (µg/L)	1	4.33a	< 1a	1.67a
	50	(0.33)a	(< 1)a	(< 1)a
Zn (µg/L)	1	73.33a	20.00a	33.33a
	50	(203.33)a	(60.00)b	(14.14)b
pH (su)	1	9.75	6.78	7.50
	5	8.24	7.06	7.20
	10	7.67	7.72	7.70
	50	7.63	7.72	7.68
Electrical Conductivity (dS/m)	1	2.72	2.99	3.51
	5	2.60	2.60	2.57
	10	2.31	2.26	2.27
	50	2.01	1.99	2.36

Table 6. Analytical results (means) of Tempe cell leachate from Phase II. Dissolved metal values are denoted in brackets (). Different letters following means indicate that they are significantly different (p = 0.05).

Parameter	No-treatment	7.62 cm Ferric oxide	15.24 cm Ferric oxide
Dissolved Arsenic (Fg/l)	242	78	51

Table 7. Dissolved arsenic concentrations in leachate from amended tailings with 0, 7.62 cm and 15.24 cm thick basal layers of ferric oxide.

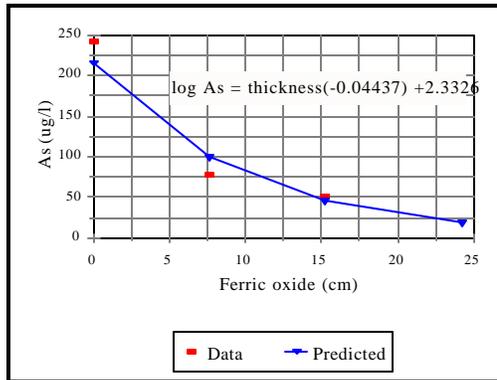


Figure 2. Log regression model for predicting ferric oxide thickness.

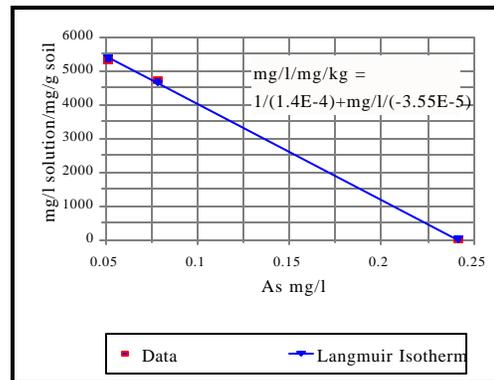


Figure 3. Langmuir isotherm model of arsenic adsorption data.

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