

Use of Steel Slag Leach Beds for the Treatment of Acid Mine Drainage

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ABSTRACT

In the past passive treatment of acid mine drainage (AMD) has relied almost solely on the dissolution of limestone to increase water pH and alkalinity and precipitate metals. However, many of these systems have met mixed success due to their susceptibility to metal precipitation or their inability to completely treat highly acidic or high flow discharges. Needed is a reliable, inexpensive alkaline source that can be applied to these highly acidic, high flow discharges. Laboratory and field studies indicate that high alkaline steel slag may be the solution.

Steel slags with varying neutralization potentials were leached with AMD of a known quality using an established laboratory procedure. Leaching continued for 60 cycles and leachates were collected after each cycle. Leachates were analyzed for pH, alkalinity/acidity, Fe, Al, Mn, Ca, Mg, Ag, As, Ba, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, V, Zn. Results from the tests showed that very little of the metals in the leachates originated from slag leaching, even under acidic conditions. These results indicate that many metals present in slag may be bound in insoluble forms that remain stable under a variety of pH ranges.

In October 2000 steel slag leach beds were constructed at the abandoned McCarty Highwall site in Preston County, West Virginia. The leach beds were constructed as slag check dams below limestone-lined settling basins. Acid water was captured in limestone channels and into the basins where it would leach through the slag dams and discharge into an unnamed tributary of Beaver Creek. Since installation the system has been consistently producing net alkaline, pH 10 water. Samples taken 1/2 mile downstream, after the treated water encounters several other acid seeps, show that water at this point is still net alkaline and has stabilized at a neutral pH.

INTRODUCTION

Slag is the fused product formed by the action of a flux upon the impurities of an ore (US Steel, 1964). In the steelmaking process it is formed during the addition of limestone,

dolomite or lime to the molten iron ore. These calcium compounds complex with aluminum, silica, phosphorus and other impurities in the iron to form slag. What results is a much stronger steel product and a pile of amorphous, glass-like, calcium aluminosilicate oxides, more commonly called slag. The slag floats to the top of the melt and is poured off into piles for disposal. Due to its extremely high temperature, approximately 2700 degrees Fahrenheit, it cools almost immediately.

Slag is considered a waste product in the production of steel, however, it has various uses outside of the metal industry. It is used extensively in the construction industry where it is used as a component of concretes, pavements and roofing granules (US Steel, 1964). In addition, steel slags have a high neutralization potential (Table 1) and can be used as an alkaline addition to acid producing materials.

Table 1: Neutralization potential of various basic steelmaking slags.

Slag Identification	Neutralization Potential	
	Tons/1000 tons	%
Weirton c-fines	770	77%
Mingo c-fines	665	66%
Mingo Cool Springs	628	63%
Waylite	421	42%
Fairfield	469	47%

Since slag is formed at such high temperatures most compounds with lower boiling points have been driven off. Any residuals of these compounds, such as sulfur, selenium, carbon, cadmium, lead, copper and mercury, are typically encased within the slag's glassy matrix. Since the chemical bases of slag consists mostly of lime, magnesia and other basic compounds, leaching of this material results in the liberation of high concentrations of alkalinity to the dissolving fluid. This can drive the pH of the fluid to 10 or 11 (Ziemkiewicz and Skousen, 1998). However, the lime in slag, unlike ordinary agricultural lime, is in loose chemical combination with silica, iron and manganese. Slag does not "burn" like agricultural lime nor revert to carbonates. Therefore, slag remains in a stable, almost neutral, form where it will produce alkalinity over long periods of time until exhausted (US Steel, 1964).

Since most steel slags contain heavy metals there has been some concern with the potential of these metals to leach out under acidic conditions. Therefore, before utilizing slag in the field for AMD treatment it is important to determine the leachability of these metals in a controlled laboratory test. In Spring 2000 the National Mine Land Reclamation Center developed a method for assessing the leachability of heavy metals from steel slag (Ziemkiewicz and Simmons, 2000). The Mine Water Leaching Procedure (MWLP) is a modification of USEPA Method 1311 Toxicity Characteristic Leaching Procedure (TCLP) and USEPA Method 1312 Synthetic Precipitation Leaching Procedure (SPLP) which were already in use for the determination of the mobility of organic and inorganic analytes present

in liquid, solids and wastes (U.S. Environmental Protection Agency, 1992 and U.S. Environmental Protection Agency, 1994).

MINE WATER LEACHING PROCEDURE

Objective

The objective of this procedure was to determine the ability of high alkaline steel slags to add alkalinity to and remove metals from acidic mine waters. In addition, the study monitored the occurrence of metals in the leachate to quantify the leachability of trace and heavy metals in the slag.

Strategy

This objective was accomplished through the systematic addition of fresh acid mine drainage (AMD) to each slag sample until all alkalinity was exhausted from the slag and pH of the leachate was at similar levels as the original mine water.

Selection of slag and water

Slags used in this study included Mingo c-fines and Mingo Cool Springs from Junction, Ohio, Waylite from Johnstown, PA and Fairfield from Fairfield, AL. The compositions of these slags vary slightly due to the impurities in the iron ore and limestone (or dolomite) used in their production. The slags were sieved to less than 1/8 inch particle size and had neutralization potentials of 421-665 tons/1000 tons (see Table 1).

Acid mine drainage was collected from the T&T underground coal mine site in Preston Co. WV. This is strongly acidic water that is very high in metals. It is typical of underground coal mine drainage from the Freeport coal seams in Northern WV (Table 2).

Table 2: Water quality of TBT Mine discharge.

Sample Identification	pH	Alkalinity (mg/L)	Acidity (mg/L)	Net Alkalinity (mg/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)	Ca (mg/L)	Mg (mg/L)
T&T mine discharge	2.71	0	613.4	-613.4	90.5	37.7	1.8	247.4	53.5

Sample Identification	Cu (mg/L)	V (mg/L)	Zn (mg/L)	Hg (mg/L)	Sb (mg/L)	As (mg/L)	Se (mg/L)	Pb (mg/L)
T&T mine discharge	0.6572	0.0609	2.035	0	0.2954	0.1	0.4918	0.1963

Sample Identification	Cd (mg/L)	Cr (mg/L)	Ba (mg/L)	Be (mg/L)	Ni (mg/L)	Ag (mg/L)	Tl (mg/L)	SO4 (mg/L)
T&T mine discharge	0.0145	0.0921	0.0196	0.0278	0.5009	0.0346	0.4822	7146

Experimental Procedure

100 g of slag was weighed out into 3 labeled, plastic containers (12 total). which had been washed and acid rinsed. The containers were labeled as follows...

1. Mingo c-fines Rep #1
Rep #1

7. Wayiite

- | | |
|-------------------------------------|-----------------------|
| 2. Mingo c-fines Rep #2
Rep #2 | 8. Waylite |
| 3. Mingo c-fines Control
Control | 9. Waylite |
| 4. Mingo Cool Springs Rep #1 | 10. Fairfield Rep #1 |
| 5. Mingo Cool Springs Rep #2 | 11. Fairfield Rep #2 |
| 6. Mingo Cool Springs Control | 12. Fairfield Control |

2 liters of AMD were added to containers labeled Rep #1 and Rep #2 and 2 liters of deionized water were added to the Control containers. Amounts added were determined from the following equation from EPA SW846 Method 1311:

$$\text{Weight of Extraction Fluid} = \frac{(20) \times (\% \text{ Solids}) \times (\text{Weight of sample})}{100}$$

*The weight of extraction fluid determines the amount of extraction fluid, in this acid mine drainage, to use in the leaching procedure. It is typically 20 times the weight of the solid sample, however, the equation includes a term (% solids/100) to correct for the weight of water in a slurry sample.

The containers were then sealed with Parafilm and the lids were screwed on to ensure a tight fit and discourage leaking. The containers were then tightened down onto an end-over-end rotating platform and agitated for 18 hours at 30 rpm.

Sampling Procedures

Sampling was performed following each 18 hr agitation cycle. Contents of each container were filtered through 0.7 um acid rinsed TCLP filter paper using a stainless steel pressure filtration unit at or below 20 psi. Solids and filtrates were then handled separately.

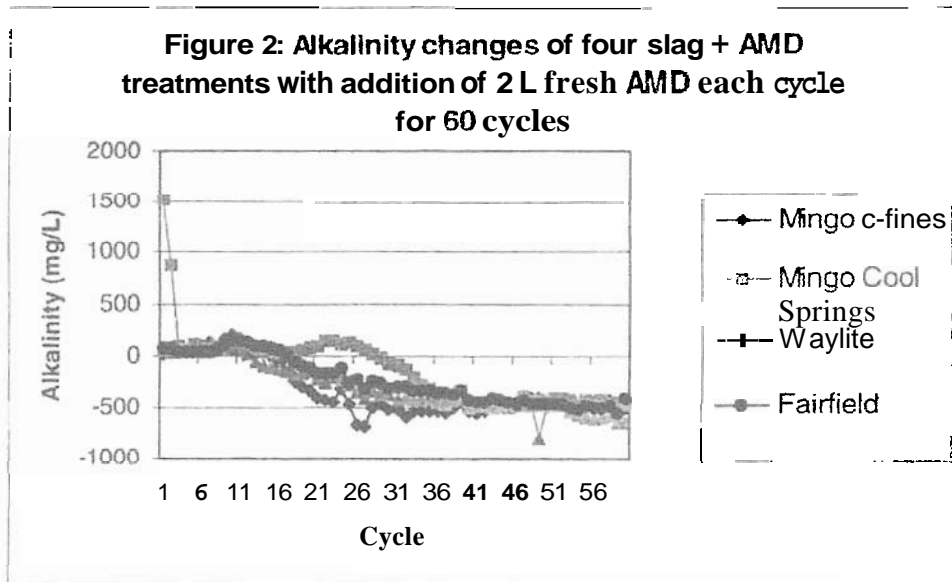
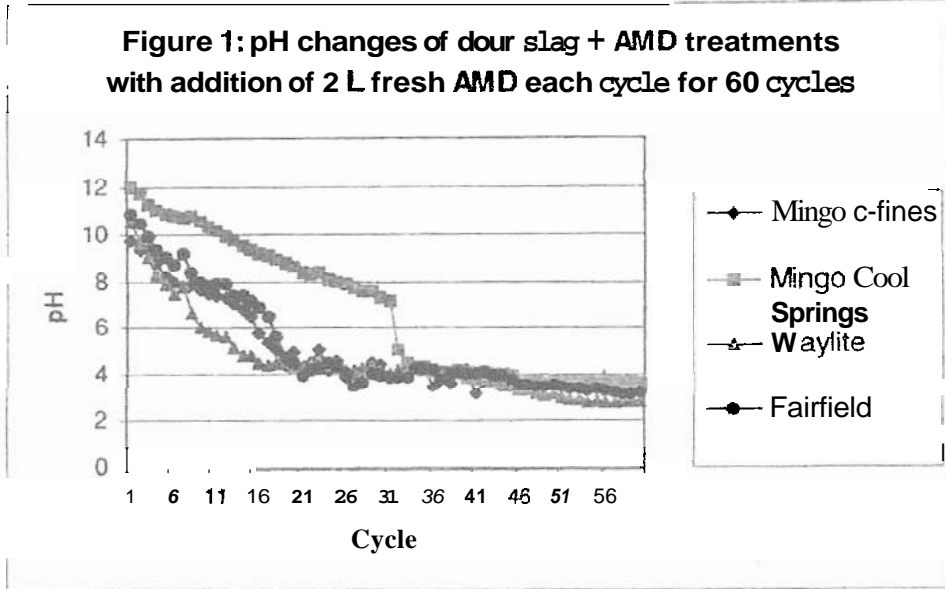
Solids were rinsed back into corresponding containers using 2 "fresh" liters of AMD for Reps #1 and #2 and 2 liters of deionized water for the controls. These containers were then sealed and placed back onto the rotating platform for another 18 hr cycle.

Filtrate was collected into 250 ml sample bottles for laboratory analysis. The initial sample set and every fifth sample sets were collected for pH, alkalinity, acidity Fe, Al, Mn, Ca, Mg, Ag, As, Ba, Be, Cd, Cr, Cu, Hg, Pb, Ni, Sb, Se, Tl, V, and Zn using 2- 250ml samples of filtrate (1-acidified for metals and 1-nonacidified for pH, alkalinity and acidity). All other sample sets were analyzed for pH, alkalinity and acidity using only 1-250 ml nonacidified sample

Results of Laboratory Leachings

Figures 1 and 2 show the pH and alkalinity evolution of the four leachates over the 60-cycle period. Mingo c-fines, Waylite and Fairfield leachates followed similar trends for pH and alkalinity. The pH of these leachates fell from 10.81 (Fairfield), 10.57 (Waylite) and 9.75

(Mingo c-fines) to just above pH 4.0 by cycle 21. The pHs dropped only slightly after cycle 21 and were near 3.5 by the end of the leaching period (cycle 60). Alkalinities of these three leachates also followed similar trends. Starting out at 16.48 mg/L (Mingo c-fines), 54.2 mg/L (Waylite) and 61.97 mg/L (Fairfield), leachate alkalinities rose slightly during the first



10 cycles and then fell to become net acid between cycles 13 and 18. As fresh acid mine drainage was added in each new cycle, the leachates become increasingly more acidic, ending between 404 and 652 mg/L in cycle 60. The initial leachate from the Mingo Cool Springs slag was more than 1 pH unit higher (11.97) than the other three slag leachates and contained over 1500 mg/L of alkalinity. Leachate pH fell steadily over the next 31 cycles to

Table 3 also shows that, although Ag, V, Ba and Mn leached from the slags during some leaching cycles, the overall trend for every metal in this analysis **was** sequestration. This is due to the addition of fresh acid mine drainage each cycle. Therefore, the slags were not coming into contact with a single volume of water containing various amounts of metals, they were reacting with 60- 2L volumes of acid mine drainage. For example, the raw AMD contained 0.0196 mg/L of barium, or 0.0000392 g of Ba in 2 Liters. Each new addition of AMD to the slag adds another .0000392 g of Ba to the system. In the case of Mingo c-fines, barium concentrations in the leachate were higher than that of the original AMD, therefore the increase in barium could be attributed to the slag. However, in subsequent cycles the leachate concentration was lower than the AMD (Table 4). This showed that not only was the slag not leaching its metals to the water in the subsequent cycles, it was actually sequestering metals from the AMD. Figure 3 shows the percentage of metals in the AMD that were sequestered by the slag, and therefore, removed from the water. Nearly 100% of Fe, Al, Cu, Zn, Pb, Cd, Be, Ni and Ti were removed from the AMD. Furthermore, percent metal removal **was** never less than 83%.

Figures 4 and 5 show release and sequestration of manganese, a metal released from 3 of the 4 slags, and zinc, which **was** not released from any of the 4 slags. "Negative grams" represent a release of metals due to the addition of AMD to the slag and "positive grams" represent sequestration of AMD metals in the slag. The increase of sequestration with leaching cycles corresponds to the addition of metals into the system with each addition of fresh acid mine drainage. Manganese was released in three of the four slags. In Mingo c-fines manganese was released early in the leaching period. However, Mingo Cool Springs and Waylite showed a release of manganese mid-way through the leaching period.

Table 4: Import of barium from AMD addition vs barium in the leachate and subsequent sequestration (+) or release (-) of barium from Mingo c-fines slag every five cycles for 60 cycles. Percent sequestered represents the percent of metals added to the system from the AMD that are sequestered by the slag.

Import		Leachate		Sequestered		
Cycle	(grams)	Cycle	(grams)	Cycle	(grams)	%
1	3.92E-05	1	0.000087	1	-4.78E-05	-121.9%
5	0.000196	5	3.93E-05	5	0.000157	79.9%
10	0.000392	10	4.41E-05	10	0.000348	88.8%
15	0.000588	15	0.000124	15	0.000464	78.9%
20	0.000784	20	0.000105	20	0.000679	86.7%
25	0.00098	25	8.87E-05	25	0.000891	90.9%
30	0.001176	30	7.74E-05	30	0.001099	93.4%
35	0.001372	35	8.04E-05	35	0.001292	94.1%
40	0.001568	40	0.000073	40	0.001495	95.3%
45	0.001764	45	0.000154	45	0.00161	91.3%
50	0.00196	50	8.71E-05	50	0.001873	95.6%
55	0.002156	55	8.06E-05	55	0.002075	96.3%
60	0.002352	60	8.24E-05	60	0.00227	96.5%

Figure 3: Percentage of metals in AMD that were sequestered in the slag.

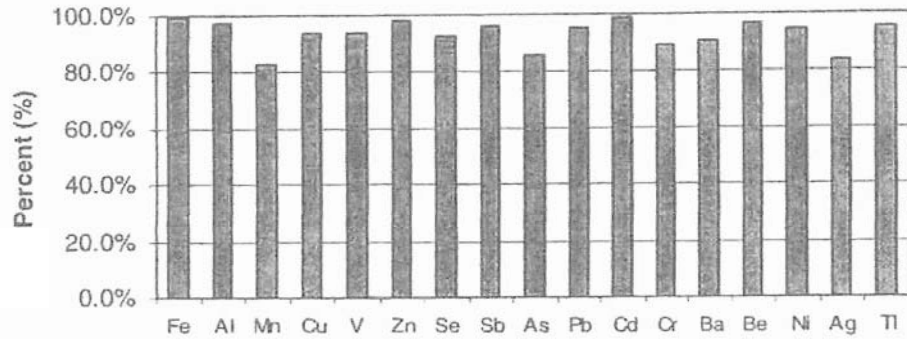


Figure 4: Grams of Mn sequestered (+) or released (-) due to slag addition to AMD.

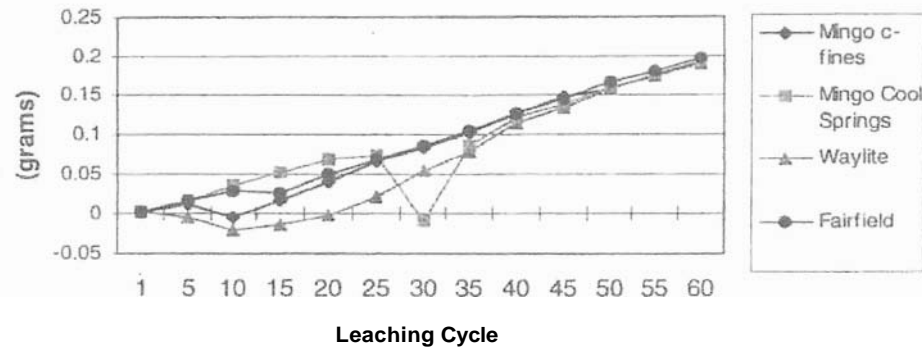
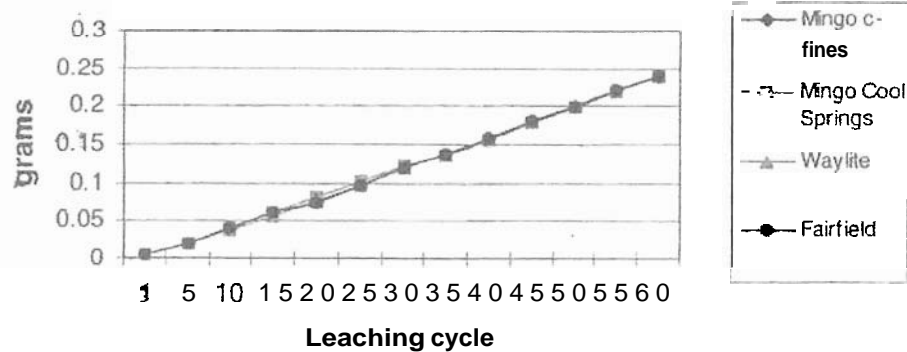


Figure 5: Grams of Zn sequestered (+) or released (-) due to slag addition to AMD.



THE MCCARTY HIGHWALL PROJECT

Field Demonstration

The McCarty Highwall is an abandoned surface mine site located about 3 miles Southeast of Bruceton Mills in Preston County, West Virginia. Pre-law contour mining of the Bakerstown and Freeport coal seams have altered both the surface topography and water quality of this region. An abandoned highwall and its accompanying pit lake were discovered at the northeast corner of the site. Sampling of the pit lake revealed that this water was pH neutral and net alkaline. However, seeps originating within the spoil material downslope of the pit lake were acidic, with pHs between 3.7 and 3.9, average acidities of 26 mg/L, and average concentrations of iron, aluminum and manganese of 0.6 mg/L, 3.6 mg/L, and 3.3 mg/L, respectively. Prior to construction at McCarty, water seeping out along an old spoil pile was flowing into a channel and mixing with a second spoil seep approximately 500 ft downstream. These two seeps formed a small acid stream that flowed south into Beaver Creek. Along the way the stream picks up several other small AMD seeps.

Due to the acidity of the on-site AMD sources and the presence of additional acid sources downstream, limestone treatment was insufficient. A stronger alkalinity source was needed: one that would raise the alkalinity of the on-site water to levels that would neutralize additional AMD entering the stream downstream. In addition, it needed to be inexpensive and last for at least 10 years without maintenance. Earlier laboratory studies with steel slag indicated its suitability for such situations (Ziemkiewicz and Skousen, 1998).

In October 2000, a series of open limestone channels (OLCs) and steel slag leach beds were installed downstream of seeps 1 and 2. Figure 4 shows the placement of the OLCs and leach beds and the amounts of limestone and slag used in each. All four OLCs were constructed of a limestone sand liner and 6-8" limestone rocks. The leach beds consisted of a settling basin and steel slag check dam. Both check dams were formed from approximately 150 tons of Weirton c-fines steel slag (Weirton Steel, Weirton, WV. NP = 77%) and rip rapped along the back with 6-8" limestone rocks. A 200 ft open limestone channel (OLC #1) was constructed from the upper spoil seep to the edge of the first settling basin. A secondary OLC (OLC #1b) was constructed to the left of OLC #1 to carry AMD from an intermittent spoil seep to the first basin. Water leaches from the basin through the center of a steel slag check dam and enters a 300 ft open limestone channel (OLC #2). OLC #2 exits into a limestone gravel area along the edge of the second settlement basin. AMD from the downstream seep flows from the left of basin #2 through a 100 ft open limestone channel (OLC #3) and exits into the gravel area at the edge of the second settling basin. Water enters into settling basin #2 from OLCs #2 and #3 and exits the system through a second steel slag check dam. This water then flows north into Beaver Creek, picking up several additional acid seeps along the way.

Results of Steel Slag Leach Beds

Water samples were collected throughout the system and downstream of the second leach bed monthly for nine months. Samples were then analyzed for pH, acidity, alkalinity, Mg, Ca, Fe, Al, Mn, SO₄, Sb, As, Ba, Be, Cd, Cr, Pb, Hg, Se, Ag, Cu, Ni, Tl and Zn. Results have shown that the system is neutralizing all the acidity of the influent water. In fact, it is

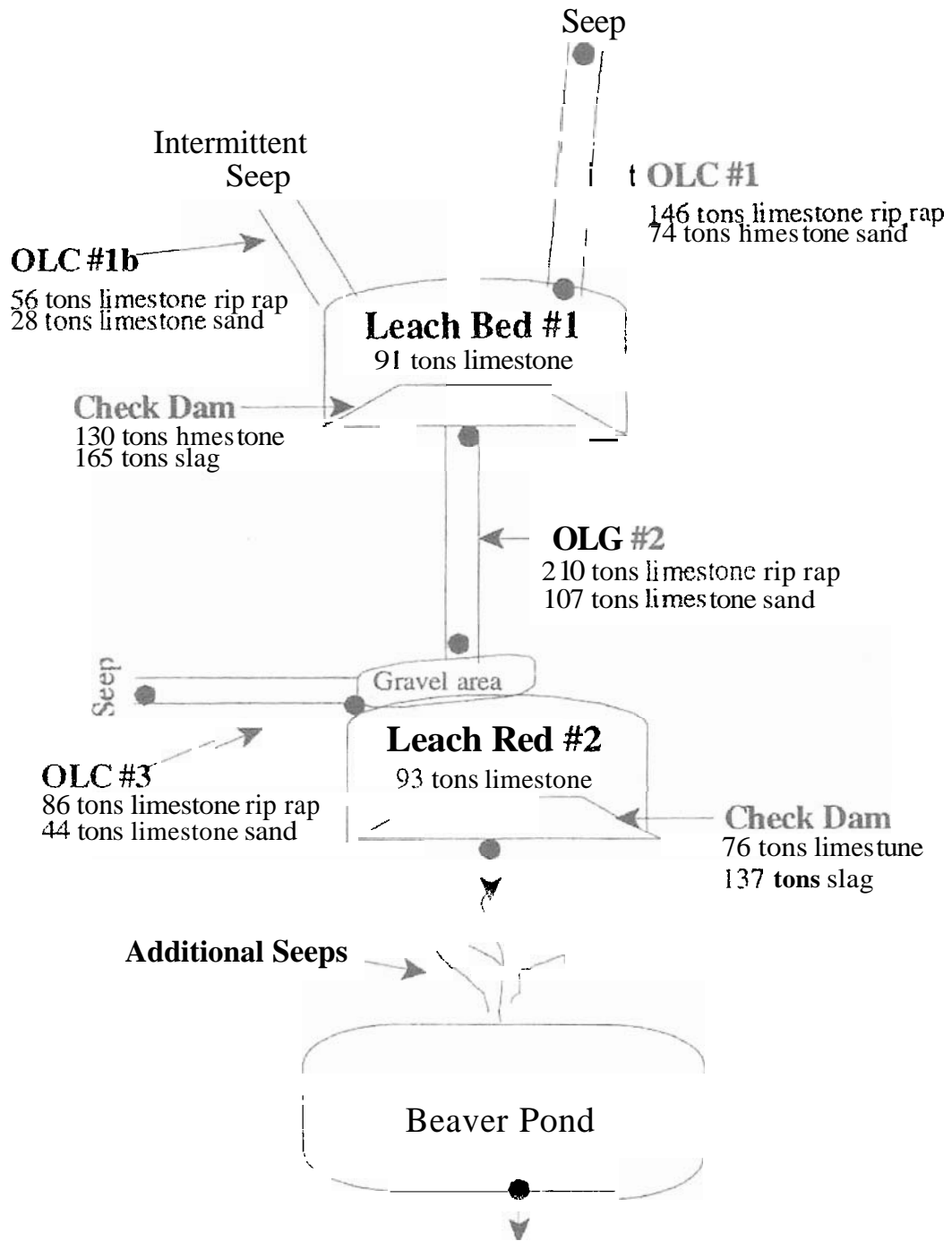


Figure 6: McCarty Highwall Treatment area.

producing net alkaline water at its discharge and ½ mile downstream (Table 5). In addition, metal leaching does not appear to be a problem. Out of the 18 metals analyzed, only 11 were present in the discharge water. Of these 11 metals, only Ra, Cr, Cd and V were higher in the discharge water than in the raw AMD. Increases in these four metals could be attributed to the slag. However, none of these metals exceeded the USEPA's drinking water standards (US Environmental Protection Agency, 1995).

Table 5: pH, alkalinity and metal concentrations present in discharge water and 1/4 mile downstream. Water was analyzed for Sb, As, Ba, Be, Cd, Cr, Pb, Hg, Se, Ag, Cu, Ni, Ti, V and Zn. However, only metals listed in the table were present in discharge and downstream samples. Concentrations listed are averages of the five most recent sampling occasions. Numbers underlined exceed USEPA drinking water, public water supply or human health limits. Number in bold face exceed raw AMD concentrations.

sampling station	field pH	Net alkalinity (mg/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)	Ba (mg/L)	Cd (mg/L)
EPA Drinking Water Standards			1.5	-	1	2	0.005
Raw AMD	4.1	-2.3	<u>10.0</u>	1.2	<u>1.5</u>	0.016	0.000126
Leachbed #2 Out	9.2	30.7	0.4	0.7	1.2	0.066	0.000
Downstream	6.5	24.4	0.5	0.3	0.5	0.017	0.0004
sampling station	Cr (mg/L)	Se (mg/L)	Cu (mg/L)	Ni (mg/L)	V (mg/L)	Zn (mg/L)	
Water Quality Limit	0.1	0.05	1	0.51	-	0.6	
Raw AMD	0.000	0.00141	0.001	0.127	0.000	0.144	
Leachbed #2 Out	0.002	0.000	0.000	0.054	0.0004	0.101	
Downstream	0.038	0.0009	0.000	0.011	0.000	0.020	

CONCLUSION

The Mine Water Leaching Procedure was developed to quantify the potential of steel slags to leach metals into surface waters under acidic conditions. The potential of these slags to leach metals into the surrounding environment would determine its suitability for treatment of acid mine waters. Slags were leached with 3 Liter volumes of acid mine drainage for 60 cycles. The leachates became acidic between cycles 13 and 29. The slag remained in an acidic environment for 47-31 cycles to simulate the long-term effects of an acid environment on slag leaching.

The results from these tests indicate that minimal leaching may occur from the slag and that most leaching that occurs will do so in the early phases of treatment, when pH is at its highest. Additionally, we expect that, although some leaching may occur early on, the long-term trend of the project will be sequestration of metals in the slag.

Based on the results of the MWLP, a field demonstration was developed to determine the suitability of steel slag for acid mine drainage treatment at an abandoned surface mine in Preston County, West Virginia. At this site steel slag leach beds were constructed downstream of two acid seeps to increase alkalinity of and remove metals from the water

Water was sampled throughout the system, as well as, downstream of the system and analyzed monthly for pH, acidity, alkalinity, Mg, Ca, Fe, Al, Mn, **Ag, As**, Ba, Be, Cd, Cr, Cu, Hg, NiPb, Se, Sb, **Tl**, V, Zn and sulfate. Results were then compared to the raw AMD to determine the amount of treatment and metals leaching from the steel slag.

Concentrations of barium, chromium and vanadium were higher in the system outflow than in the raw AMD. This is not surprising since barium and vanadium were the two metals that leached from all four slags during the laboratory leaching procedure. Unlike the laboratory leaching, it appears that chromium is also leaching from the Weirton slag. However, there does not appear to be a trend of increasing release of any metal from the slag. In addition, at no time have the concentrations of metals in the effluent waters exceeded the EPA's drinking water standards. Therefore, we do not expect these metal concentrations to be detrimental to the downstream surface waters.

Due to the relatively new construction of the McCarty leach beds, monitoring will continue at this site to determine the long-term performance of the slag and to identify metals leaching from the slag. Work also continues to identify other potential AMD impacted sites that could benefit from slag-based passive treatment systems.

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