

Technical Article

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

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Abstract. Steel slag from the Waylite steel-making plant in Bethlehem, Pennsylvania was leached with acidic mine drainage (AMD) of a known quality using an established laboratory procedure. Leaching continued for 60 cycles and leachates were collected after each cycle. Results indicated that the slag was very effective at neutralizing acidity. The AMD/slag leachates contained higher average concentrations of Ba, V, Mn, Cr, As, Ag, and Se and lower average concentrations of Sb, Fe, Zn, Be, Cd, Tl, Ni, Al, Cu, and Pb than the untreated AMD. Based on these tests, slag leach beds were constructed at the abandoned McCarty mine 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 directed into basins to leach through the slag dams and discharge into a tributary of Beaver Creek. Since installation in October 2000, the system has been consistently producing net alkaline, pH 9 water. The treated water is still net alkaline and has a neutral pH after it encounters several other acidic seeps downstream.

Key words: Acid mine drainage, Beaver Creek, check dam, leach beds, leaching, metal sequestration, mine water leaching procedure, open limestone channel, steel slag, West Virginia

Introduction

Acid mine drainage (AMD) forms when sulfide minerals, particularly pyrite and marcasite, are exposed to oxidizing conditions during excavation activities, such as mining and highway construction. In the presence of oxygen and water, sulfide minerals oxidize to form sulfate-rich and often metal-laden drainage (Skousen 1996). "Untreated AMD flowing into streams can severely degrade both habitat and water quality, often producing an environment devoid of most aquatic life and unfit for desired uses" (Kimmel 1983). In addition, AMD can be toxic to vegetation and can reduce the potability of water supplies (Earle and Callaghan 1998).

Various active and passive water treatment techniques have been developed during the last

several decades to abate or control AMD. Active systems require the systematic and long-term addition of various alkaline chemicals, such as ammonia, hydrated lime or caustic soda. These systems are often very effective at neutralizing acidity; however, they are typically very expensive and require long-term commitments of manpower and maintenance. In contrast, passive treatment systems are less expensive and require very little maintenance.

Passive treatment of AMD has largely relied on the dissolution of limestone to increase pH and alkalinity and precipitate metals. However, limestone is susceptible to armoring due to metal precipitation and its effectiveness in highly acidic or high flow discharges is limited. Laboratory and field studies indicated that highly alkaline steel slag could be a reliable, inexpensive alternative in such situations (Ziemkiewicz and Skousen 1998).

Slag is formed during the steel-making process by 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. What results is a much stronger steel product and glass-like, calcium aluminosilicate oxides, commonly called slag. The slag floats to the top of the melt and is poured off into piles for disposal. It cools very quickly from an extremely high temperature, approximately 1482° C (2700° F).

Slag is considered a waste product but it has various uses outside of the metal industry. It is used extensively in construction 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 to add alkalinity to acid-producing materials.

Since slag is formed at such high temperatures, most compounds with relatively low boiling points have been driven off. Residuals of compounds such as sulfur, selenium, carbon, cadmium, lead, copper, and mercury are typically encased within the slag's glassy matrix. Slag also contains lime, magnesia and other alkaline compounds; these can leach out, increasing the pH of the water to 10 or 11 (Ziemkiewicz and

Table 1. Neutralization potential (NP) (g CaCO₃ equivalent/Kg of slag) of various basic steelmaking slags; NP determined using the Sobek (1978) method

Slag Identification	NP	%
Weirton c-fines	770	77
Mingo c-fines	665	66
Mingo Cool Springs	628	63
Waylite	421	42
Fairfield	469	47

Skousen 1998). However, slag does not convert to carbonate and release carbon dioxide like lime can; therefore, slag can continue to produce alkalinity over long periods of time (US Steel 1964).

Since most steel slags contain heavy metals, there has been some concern about the potential of these metals to leach out under acidic conditions. Therefore, before utilizing slag in the field for AMD treatment, it was important that we determine the leachability of these metals in a controlled laboratory test. However, traditional tests, such as the Toxicity Characteristic Leaching Procedure (TCLP) (U.S. EPA 1992) and Synthetic Precipitation Leaching Procedure (SPLP) (U.S. EPA 1994) may only account for relatively fast reactions that take place in a single leaching process (Yan et al. 2000). To ensure the safety of using slag in the field, its long-term reactivity had to be determined. To accomplish this, the National Mine Land Reclamation Center developed a Mine Water Leaching Procedure to determine the steel slag's acid neutralizing potential, and identify the potential risk of metal release from the steel slag into surrounding aquatic environments (Ziemkiewicz and Simmons 2000). This was accomplished by the systematic addition of fresh AMD to each slag sample until all of the alkalinity was exhausted and the leachate pH was similar to that of the original mine water.

Experimental Procedure

Steel slag was collected from the International Mill Service Waylite Steelmaking Plant in Bethlehem, PA. The slag was collected from disposal piles within the plant and shipped to our laboratory, where it was sieved to less than 31.75 mm (1/8 inch) particle size and analyzed for Neutralization Potential (NP).

AMD was collected from the T&T coal mine in Preston Co., West Virginia (WV) and analyzed (Table 2). This highly acidic, metal-laden drainage water is typical of underground mines in the Freeport coal seams in northern WV. Approximately 750 L (200 gal) were collected and stored at the NMLRC

laboratory. This water was used throughout the procedure and monitored weekly for changes in pH and acidity.

One hundred g of <31.75 mm (1/8 inch) Waylite steel slag were weighed out using a Triple Beam balance (0.1 g accuracy). Two L of T&T AMD were added to two of the containers, and 2 L of deionized water were added to the Control containers. The containers were then sealed with Parafilm and the lids were screwed on to ensure a tight fit. The containers were then fastened to an end-over-end rotating platform and agitated for 18 h at 30 rpm.

Sampling followed each 18-h agitation cycle. The contents of each container were filtered through 0.7 µm acid-rinsed borosilicate glass filter paper using a stainless steel pressure filtration unit at or below 40 psi. Solids and filtrates were then handled separately. Solids were rinsed back into corresponding containers using 2 L of "fresh" AMD, or 2 L of deionized water for the control. The containers were then sealed and placed onto the rotating platform for another 18 h.

Filtrates were collected for analysis. The initial sample set and every 5th sample set were analyzed using two samples of filtrate (one acidified for metals and 1 not acidified, for pH, alkalinity, and acidity). All other sample sets were analyzed for pH, alkalinity and acidity using only one non-acidified sample.

Results of laboratory leaching

The initial leachate collected from the system contained 54.24 mg/L of alkalinity, up from -613.38 mg/L in the untreated AMD (Figure 1). Alkalinity remained steady throughout the first 11 leaching cycles, averaging 56.13 mg/L, but dropped to -67.28 mg/L by the 13th cycle. Alkalinity generation continued to decrease throughout the remaining 47 cycles. The final leachate contained -652.1 mg/L of acidity. Although alkalinity changed little during the early stages of the leaching period, pH values dropped steadily throughout the first 16 cycles at an average rate of .375 pH units per cycle (pH 10.51-

Table 2. Water quality of T&T Mine discharge water (concentrations in mg/L)

pH = 2.71	Ba = 0.0196	Fe = 90.5	Sb = 0.2954
Acidity = 613.4	Be = 0.0278	Hg = BDL	Se = 0.4918
Alkalinity = 0	Ca = 247.4	Mg = 53.5	SO ₄ = 1146
Al = 37.7	Cd = 0.0145	Mn = 1.8	Ti = 0.4822
Ag = 0.0346	Cr = 0.0921	Ni = 0.5009	V = 0.609
As = 0.1	Cu = 0.6572	Pb = 0.1969	Zn = 2.035

BDL= Below detection limits

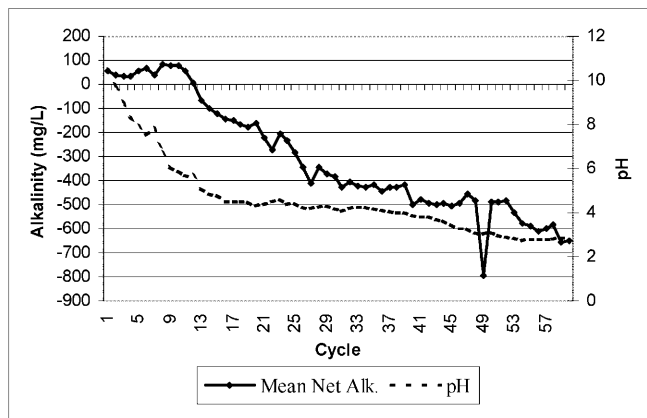


Figure 1. Mean net alkalinity and pH of leachate collected from the Waylite slag/AMD experiment

4.51). The pH continued to decrease over the remainder of the leaching period, although at a slower rate (approximately .05 pH units per cycle), and reached 2.82 by cycle 60.

Of the 18 metals analyzed, all but mercury were present at some level in the leachates. Leachate metal concentrations could be attributed to four possible sources; metal concentrations of the raw AMD, released metals from dissolution of the slag matrix, remobilized AMD metal sludge and remobilized slag metal sludge (Figure 2). To compare the amount of metal exported from the system to the amount imported into the system in the AMD, concentrations were converted to mg of metal by multiplying the concentrations in mg/L by the volume of water, which in this case was always 2 liters. Metal concentrations imported into the overall leaching system remained constant throughout the leaching period. For example, 0.2 mg of arsenic was added to the system with each 2 L addition of “fresh” AMD. Therefore, by the 5th cycle, 1.0 mg of arsenic had been imported into the system by the AMD. The total export of a metal (in mg) from the system can be calculated by adding the mg of metal in each leachate to the amount previously leached. In the case of arsenic, the initial leachate contained 0.079 mg. By the final leaching cycle (Cycle 60), 37.32 mg of arsenic had been exported.

It is difficult to identify the source of the metals in each specific leachate. However, by subtracting the metals exported from the system (in the leachate) from the metals imported to the system (in the AMD), it is possible to determine the overall effect that the slag addition had on the concentration of metals in the solid versus aqueous phase. For example, if the amount of metal exported in the leachate is less than

the amount imported by the AMD, we can assume that the slag caused the sequestration of metal into the solid phase. In contrast, if the export concentration is greater than the import concentration, then we can assume that the slag caused metals to be released from either the metal sludge or the slag.

Figures 3-18 show the cumulative metal import and export trend lines for the Waylite steel slag/T&T AMD leachate samples. Points on the graph where the import trend line is above the export line represent sequestration of AMD metals into the solid phase. Release of metals from the solid phase into the aqueous phase (leachate) is indicated where the import trend line is below the export trend line. Iron, cadmium, beryllium, zinc and antimony were sequestered into the solid phase throughout the leaching period. This means that the amount of these metals exported from the system into the leachate was always lower than what was imported into the system by the raw AMD. In contrast, barium and vanadium levels were constantly higher in the leachate than what could be attributed to the addition of metals in the AMD during each cycle. This can be attributed to the release of metals from the slag matrix. The majority of the metals showed a combination of sequestration and release. However, the point at which each trend changes from sequestration to release varies for individual metals. Manganese and chromium were initially sequestered into the solid phase. However, by the 5th (manganese) and 7th (chromium) cycles, these metals were being released into the aqueous phase. Note that these releases occurred when the pH of the leaching fluid was still circumneutral (pH 7.8-7.9). Arsenic, silver, thallium, nickel and selenium were also sequestered early in the leaching period and began to be released between cycles 15-28. Aluminum, copper and lead did not release from the solid phase until near the end of the leaching period, when the pH reached 2.9-2.7.

Table 3 is a summary of the sequestration and release trends of all the metals in this study. For those metals that showed a combined trend of sequestration followed by release, the cycle where the change occurred and the pH during this change cycle are indicated. The table also contains the average % release for each metal over the entire leaching period. Note that of the 10 metals that displayed combined sequestration/ released trends, five metals also displayed a positive average % release. Four metals (manganese, arsenic, silver, and selenium) had very high release percentages, 121.5–994.6 % greater than could be attributed to the raw AMD.

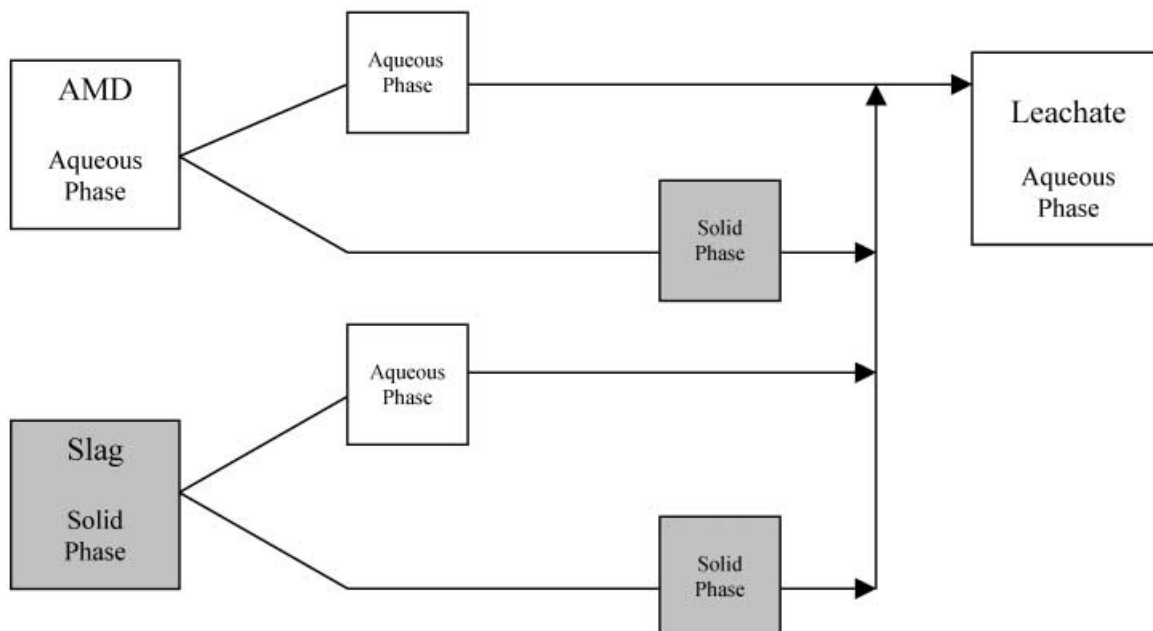


Figure 2. Diagram of the experimental system. Metals can be imported to the system from either the AMD (aqueous form) or the steel slag (solid form). Once in the system, metals can either stay in the aqueous phase, precipitate into the solid phase, or precipitated metals may resolubilize.

Metal	Trend					pH of change	Average % release
	sequestration	release	seq/release	release/seq	cycle of change		
Antimony	X						-41.4%
Iron	X						-90.4%
Zinc	X						-49.5%
Beryllium	X						-62.6%
Cadmium	X						-65.1%
Barium		X					308.5%
Vanadium		X					38.9%
Manganese			X		5	7.9	944.6%
Chromium			X		7	7.8	8.5%
Arsenic			X		15	4.8	125.4%
Silver			X		16	4.5	121.5%
Thallium			X		18	4.5	-3.4%
Nickel			X		25	4.4	-11.0%
Selenium			X		28	4.2	223.4%
Aluminum			X		52	2.9	-50.8%
Copper			X		54	2.7	-39.5%
Lead			X		54	2.7	-34.9%

Table 3. Summary of sequestration and release trends from Waylite steel slag and T&T AMD

The McCarty Field Demonstration

The abandoned McCarty surface mine is located about 5 km southeast of Bruceton Mills in Preston County, WV. Pre-law contour mining of the Bakerstown and Freeport coal seams have altered both the surface topography and water quality of this region. The water in the pit lake was determined to be pH neutral and net alkaline. However, seeps

originating within the spoil material down-slope of the pit lake were acidic, with a pH between 3.7 and 3.9, an average acidity of 26 mg/L, and average concentrations of iron, aluminum and manganese of 0.6, 3.6, and 3.3 mg/L, respectively. Prior to construction, water seeping out along an old spoil pile flowed into a channel and mixed with a second spoil seep approximately 150 m (500 ft) downstream.

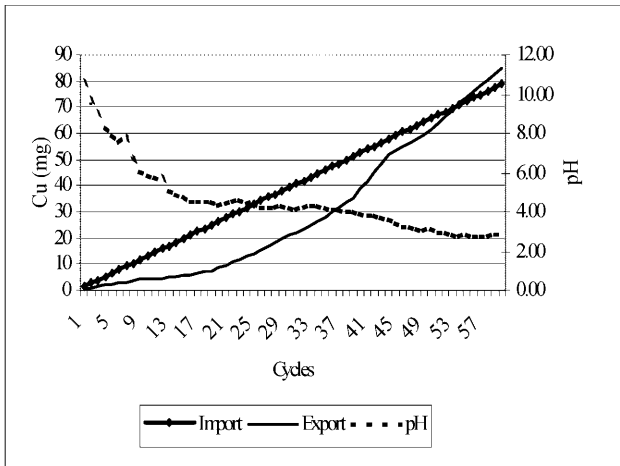


Figure 3. Copper imported with the AMD compared to Cu in the leachates

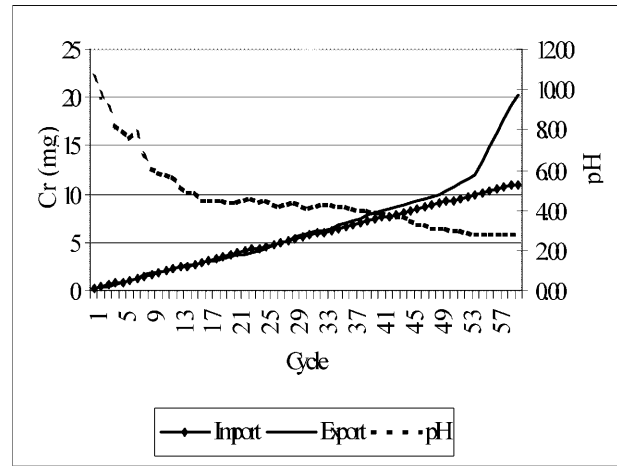


Figure 6. Chromium imported with the AMD compared to the Cr in the leachates

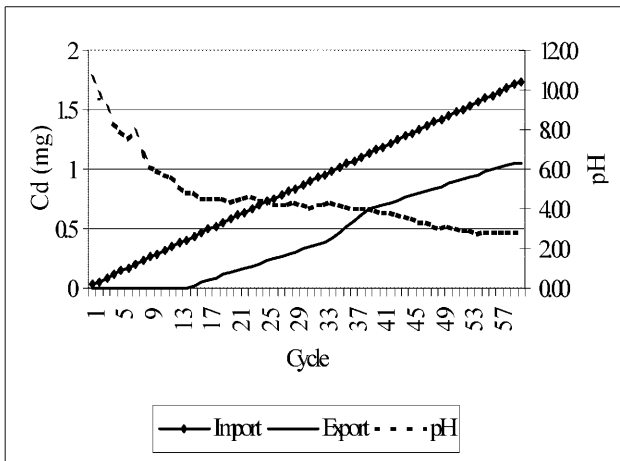


Figure 4. Cadmium imported with the AMD compared to Cd in the leachates

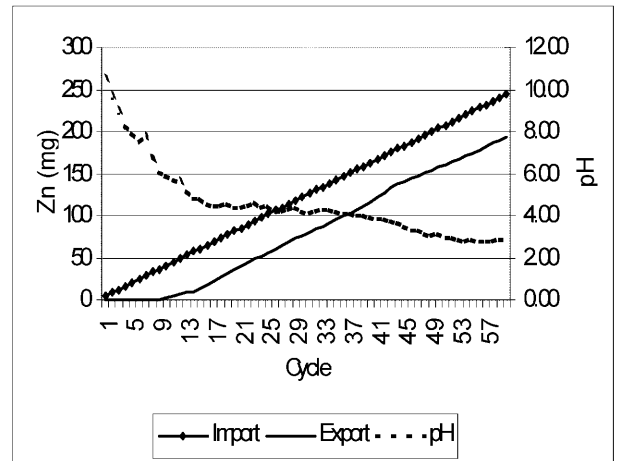


Figure 7. Zinc imported with the AMD compared to Zn in the leachates

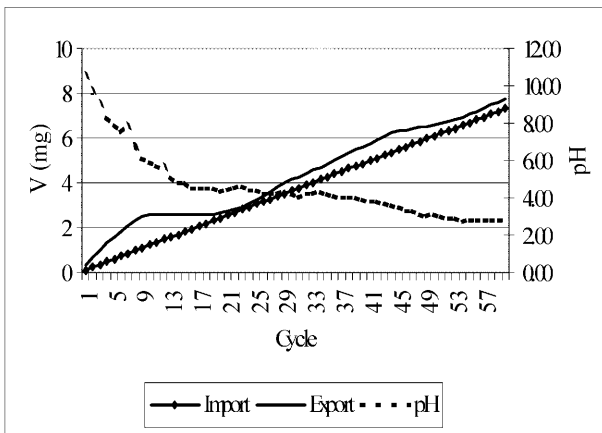


Figure 5. Vanadium imported with the AMD compared to the V in the leachates

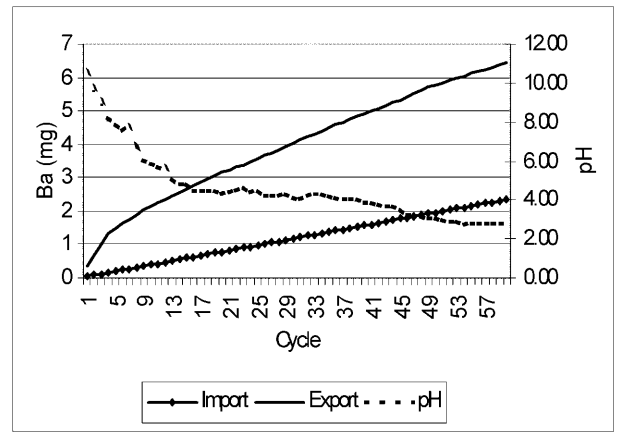


Figure 8. Barium imported with the AMD compared to the Ba in the leachates

These two seeps formed a small acid stream that flowed south, encountering several other small AMD seeps before flowing into Beaver Creek.

Due to the acidity of the on-site AMD sources and the presence of additional acid sources downstream, limestone treatment was insufficient. A stronger alkaline source was needed to raise the alkalinity of

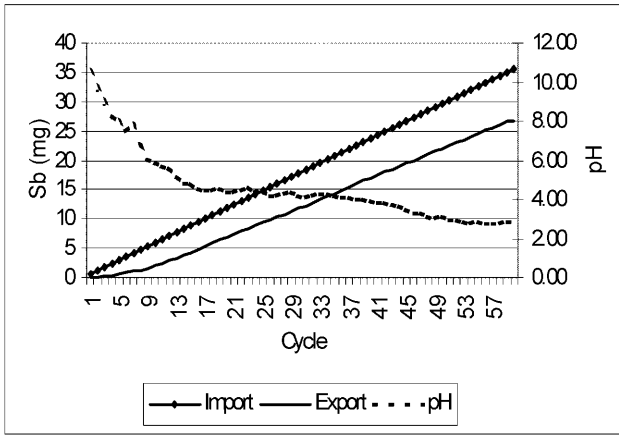


Figure 9. Antimony imported in the AMD compared to Sb in the leachates

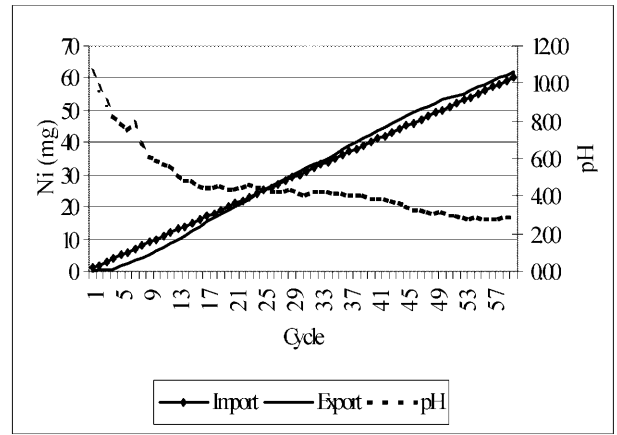


Figure 12. Nickel imported in the AMD compared to Ni in the leachates

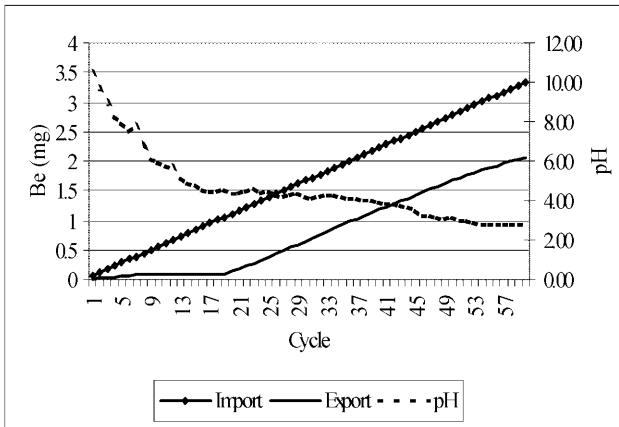


Figure 10. Beryllium imported in the AMD compared to Be in the leachates

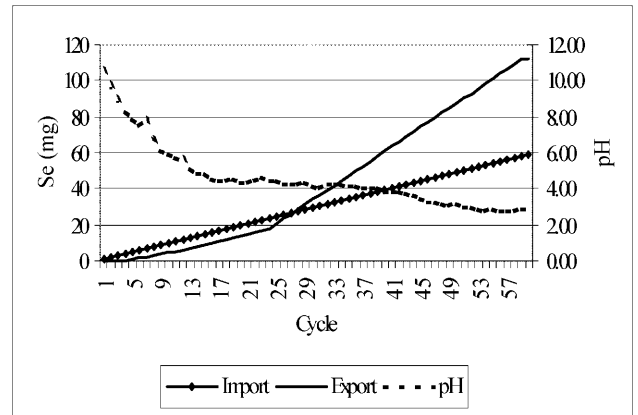


Figure 13. Selenium imported in the AMD compared to Se in the leachates

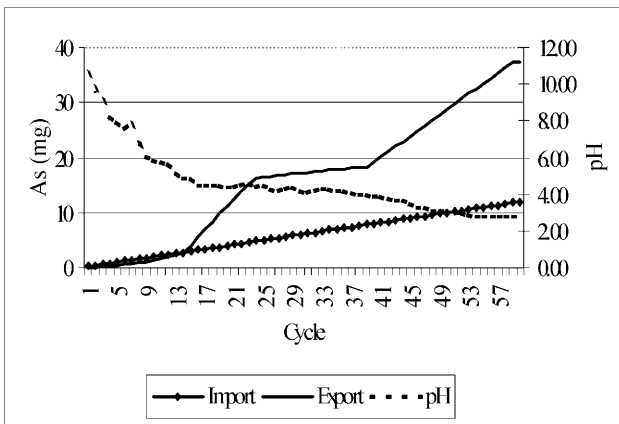


Figure 11. Arsenic imported in the AMD compared to As in the leachates

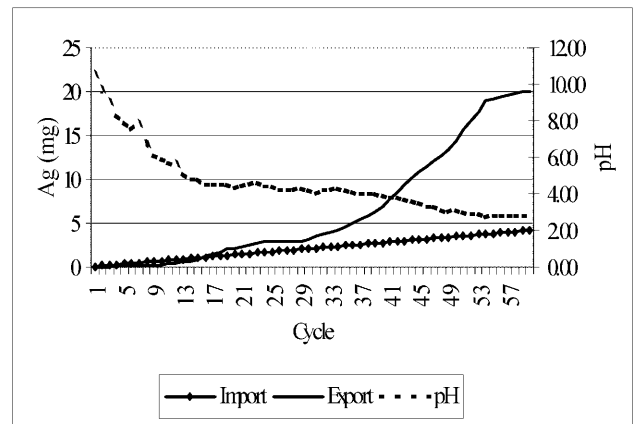


Figure 14. Silver imported in the AMD compared to Ag in the leachates

the on-site water to levels that would neutralize additional AMD downstream. In addition, economics indicated that it had to be inexpensive and last for at least 10 years without maintenance. Our earlier tests indicated the suitability of steel slag for this type of treatment.

In October 2000, a series of open limestone channels (OLCs) and steel slag leach beds were installed downstream of seeps 1 and 2. Figure 20 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

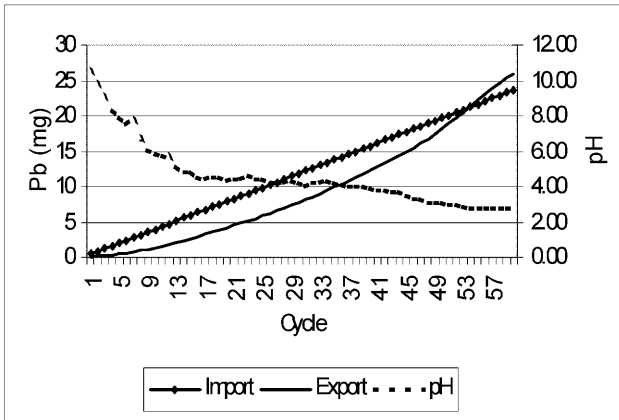


Figure 15. Lead imported in the AMD compared to Pb in the leachates

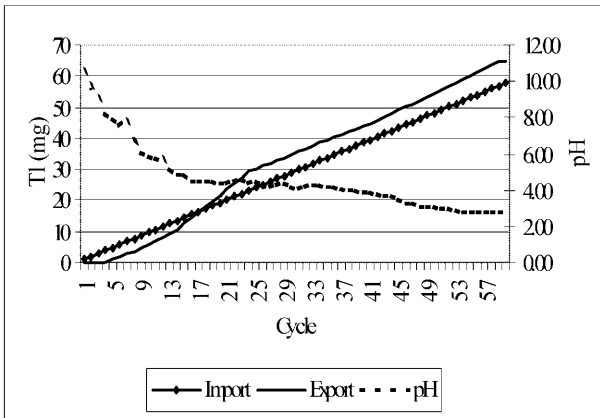


Figure 16. Thallium imported in the AMD compared to Tl in the leachates

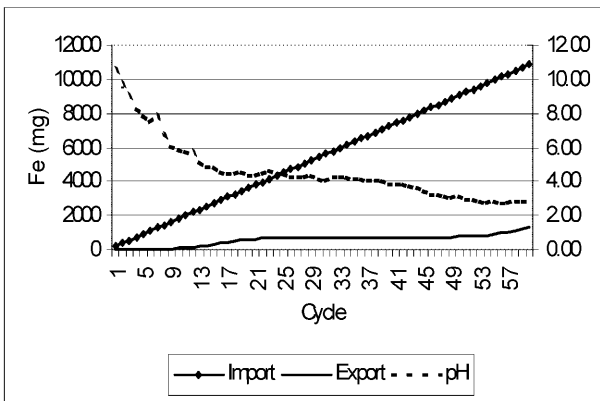


Figure 17. Iron imported in the AMD compared to Fe in the leachates

15-20 cm of limestone rocks. The leach beds consisted of a settling basin and steel slag check dam. Both check dams were formed from approximately 136,000 kg (150 tons) of Weirton c-fines steel slag (NP=77%) and rip-rapped along the back with 15-20 cm limestone rocks. A 61 m (200 ft) OLC (#1) was constructed from the upper spoil seep to the edge of

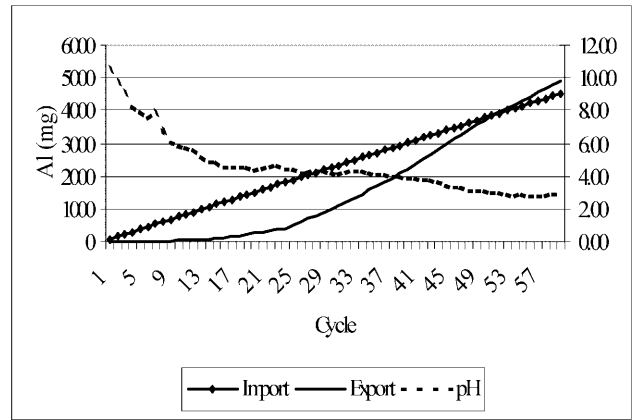


Figure 18. Aluminum imported in the AMD compared to Al in the leachates each.

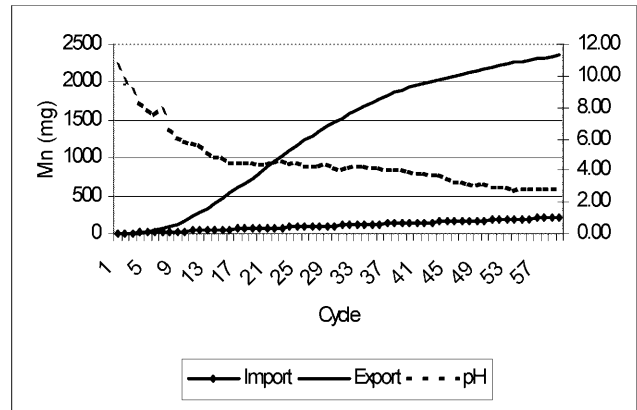


Figure 19. Mn input from the AMD compared to Mn in the leachate downstream of seeps 1 and 2.

the first settling basin. A secondary 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 91 m (300 ft) OLC (#2). Water from OLC #2 flows into a limestone gravel area along the edge of the second settlement basin.

Additional AMD flows through a 30 m (100 ft) OLC (#3) into a 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.

Water samples were collected throughout the system and downstream of the second leach bed monthly for 11 months. Initial samples collected from the slag leach beds contained extremely high concentrations of alkalinity (1479-1513 mg/L of CaCO₃ equivalent) and high pH values (11.6). However, by the fourth

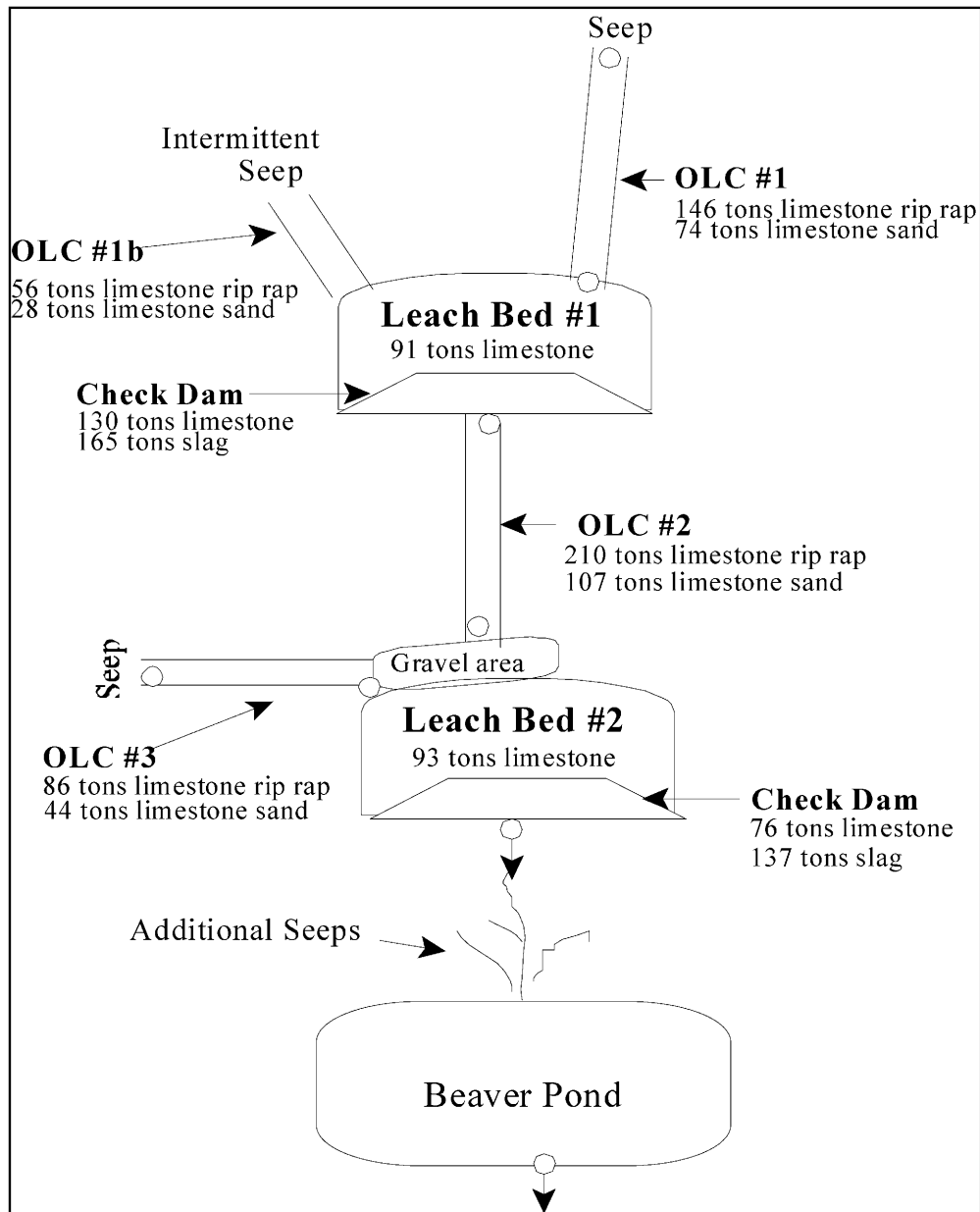


Figure 20. Diagram of the McCarty Highwall treatment site.

month, alkalinity had fallen to about 30 mg/L (pH 9.0) and has since appeared to have stabilized between 20-30 mg/L. In the first year since construction, the system has produced an average of 245 mg/L alkalinity in its discharge water (Table 4). In addition, the stream is still net alkaline approximately 1 km downstream after receiving additional acid input.

Of the 18 metals analyzed, only 11 were present in the discharge water. Of these, only antimony, chromium and vanadium were higher in the treated water than in the raw AMD. It should also be noted that no metal showed a trend of increasing concentration from month to month. This shows that

the decrease of pH and alkalinity of the leach beds is not causing an increase of metal release from the slag. Table 4 also compares the U.S. National Primary Drinking Water Standards for metals to the discharge and downstream water. Notice that no parameter exceeds these strict water quality standards.

Discussion

Barium, vanadium, manganese, chromium, arsenic, silver and selenium were identified as potential slag leaching risks during the laboratory tests. Of these metals, only chromium and vanadium has been higher in the discharge water than in the untreated AMD at the field site. However, unlike the laboratory

Table 4. Average pH, alkalinity and metal concentrations (mg/L) in untreated AMD, leach bed discharge water and ¼ mile downstream at McCarty Highwall. Numbers in bold exceed levels in the untreated AMD.

	Untreated AMD	Leach Bed #2 discharge	Downstream sampling station	EPA water quality standards
pH	4.27	9.65	7.67	
Net alkalinity	-24.1	245.12	35.01	
Fe	0.2	0.5	0.4	
Al	2.15	0.6	0.4	
Mn	3.05	0.9	0.3	
Sb	0.0017	0.003	0.004	0.006
As	0.00025	0.0001	0.0002	0.05
Ba	0.0448	0.0333	0.0485	2
Be	0.00055	0.0003	BDL	0.004
Cd	0.00045	0.0003	0.0005	0.005
Cr	0.00035	0.0046	0.0194	0.1
Pb	0.0017	0.0014	0.0012	0.015
Se	0.00185	BDL	0.0004	0.05
Ag	0.0036	0.0004	0.0001	
Cu	0.002	0.0024	0.0003	1.3
Ni	0.1411	0.0384	0.0229	
V	BDL	0.0006	BDL	
Zn	0.21945	0.0661	0.0169	

leachates, antimony concentrations were also higher in the McCarty effluent than in the raw AMD.

Overall, the results at the McCarty site have been encouraging. The limestone/steel slag system is treating all of the acidity in the AMD and has caused no harmful increase in metal concentrations in the receiving stream. However, 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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