An Alternative Alkaline Addition for Direct Treatment of Acid Mine Drainage

Jennifer S. Simmons* and Paul Ziemkiewicz
National Mine Land Reclamation Center

Abstract
The primary objective of the National Mine Land Reclamation Center has been the development and implementation of innovative passive treatment systems for the control and treatment of acid mine drainage (AMD). Historically, 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 has limited effectiveness in highly acidic or high flow discharges. Steel slag is the waste product formed when limestone or dolomite is added to molten iron ore to form steel. Calcium reacts with Si, P, Al and other impurities in the ore to form a stronger steel product and calcium alumino-silicates, which form on top of the molten iron and are poured off into piles. This material contains high concentrations of alkaline materials, particularly CaO, which can then be used to neutralize acidic materials. Several sites exist throughout the country where steel slag has been used to indirectly treat AMD through the addition of alkalinity to upstream freshwater sources. However, there was concern regarding placing these materials in acidic environments. This paper will examine two successful AMD treatment sites where steel slag has been used in the field to directly neutralize AMD.

Introduction

Acid Mine Drainage. Acid mine drainage (AMD) forms when sulfide minerals, particularly pyrite and marcasite, have been exposed to oxidizing conditions during mining and other excavation activities, such as highway construction. In the presence of oxygen and water, sulfide minerals oxidize to form sulfate-rich and often metal-laden drainage (Skousen 1995). "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 has limited effectiveness in highly acidic or high flow discharges. A reliable, inexpensive alkaline source is needed for such situations. Laboratory and field studies indicate that highly alkaline steel slag may be a solution to this problem (Ziemkiewicz and Skousen 1998).

Steel Slag.
Slag is the fused glassy compound formed by the action of a flux upon the impurities of an ore (US Steel 1964). It is formed during the addition of limestone dolomite or lime to the molten iron ore during the production of steel. These calcium compounds react with aluminum, silica, phosphorous and other impurities in the ore to form slag. The slag floats to the top of the melt and is poured off into piles for disposal, where it cools rapidly. What results is much stronger steel product and a pile of glass-like, calcium alumino-silicate oxides, more commonly called slag.

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. However, the lime in slag, unlike ordinary agricultural lime, is in loose chemical combination with silica, iron and manganese and does not "burn" nor revert to carbonates (US Steel 1964). This is an extremely important property, since it means slag can be left outside, exposed to the atmosphere, and still achieve high levels of alkalinity upon dissolution.

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.

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

Slag Identification	NP	%
Weirton c-fines	770	77%
Mingo c-fines	665	67%
Mingo Cool Springs	628	63%
Waylite	421	42%
Fairfield	469	47%

Field Demonstrations of Direct AMD Neutralization

McCarty Highwall Project. 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 1 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.

Middle Fork of Greens Run Project. The Greens Run watershed, in Central Preston, County, West Virginia is severely impacted by acid mine drainage (AMD). One of the primary acid sources to Greens Run occurs in the headwaters of the Middle Fork of Greens Run. Mining in this area has significantly altered surface topography and downstream water quality. An acidic pit lake and down slope spoil seep transport 32 to 266 tons of acid per year to the Middle Fork of Greens Run.

The two main sources of acidity at this site are an acidic pit lake and an accompanying down slope spoil seep. Extremely high concentrations of iron (approximately 887 mg/L) within the pit lake give it a deep red color, which when seen from above resembles blood. Discharge from this "Blood Lagoon" flows down a 950 ft iron-coated channel and mixes with acid water from the spoil seep (Figure 2). The mixture water then flows through two culverts under the access road and into the main channel of the Middle Fork of Greens Run. This mixed water has an average acidity of 1009 mg/L, 310 mg/L iron, 72 mg/L aluminum and 8 mg/L manganese. The water also contains small amounts of beryllium, chromium, copper, nickel and zinc.

High alkaline steel slag will be used to increase pH and alkalinity and decrease iron, aluminum and manganese concentrations of the Middle Fork of Greens Run. This will be accomplished through the construction of a steel slag leach bed within the Blood Lagoon and steel slag and limestone lined channels that transport acid water from the pit lake and spoil seep to a downstream settling basin. In addition, a treatment basin will be constructed at a spoil seep downslope of the acid lagoon. Neutralization of this seep water will be accomplished by Kish steel slag in the treatment basin. Fine slag will be added to a low area above the spoil seep. During rain events, this area collects water, which then infiltrates through the porous, acidic spoil material. This area may provide the water source for the acidic spoil seep below.

Treated water from both seeps will flow into a sump area just below the Kish slag treatment basin. This shallow sump will allow residence time for the precipitation of metals. The sump is located along the access road, which will allow for easy access if the sump would require periodic cleaning.

Water leaving the sump then flows under the access road and into a defined stream channel. Steel slag check dams will be constructed across the stream channel at 300 and 600 ft downstream of the access road. These check dams will ensure that any water circumventing the above upstream treatment systems during high flow conditions will still receive treatment before leaving the site.

Results

McCarty Highwall Project. Two years following construction, the steel slag treatment system at McCarty Highwall continues to produce net alkaline water. Water discharging from the system currently contains 41 mg/L of alkalinity and has a pH of 6.8 (Table 2). Downstream of the discharge, where the stream intercepts several other small seeps before flowing into a small beaver pond, the water remains net alkaline (21mg/L alkalinity) and has a pH of 6.3. Due to the presence of steel slag in the system, metal concentrations are monitored closely in the system discharge and at the downstream beaver pond. Most metals show a net decrease in concentration from the raw AMD. However, there have been periodic increased concentrations of both Cd and Cr in the beaver pond discharge. Cr concentrations have exceeded the National Water Quality

Criteria for Freshwater Aquatics limits on three occasions within the last two years. Cd has exceeded the limit of 0.004 mg/L on only one occasion. However, the data indicate that these are not chronic occurrences and that no metal concentrations are increasing with time or drop in pH.

Probably the most encouraging result from this project is the reestablishment of aquatic life (both benthics and fish) in Beaver Creek, the receiving stream of the McCarty discharge. Within six months following construction, benthic macroinvertebrates were discovered on substrates at the discharge of the beaver pond. In addition, there has been a remarkable improvement in numbers and species of fish in Beaver Creek, including white suckers, blacknose dace, creek shub, brook trout and mottled sculpin.

Table 2. Average water quality data from system discharge (Leach Bed 2 Out) and downstream as water exits an existing beaver pond. *Concentrations are in mg/L.*

Sampling Station	Pre-construction	Leach Bed 2 Out	Beaver Pond Out
date		10/18/2002	10/18/2002
Flow	40.2	NM	63.7
Field pH	NM	6.4	5.9
pH	3.7	6.8	6.3
acidity	45.9	0.0	0.0
est. acid	33.2	5.5	1.0
alkalinity	0.0	41.0	21.0
acid-alk	45.9	-41.0	-21.0
acid load	4.1	NM	-2.9
Mg	45.3	35.9	15.5
Ca	71.5	38.4	52.9
Fe	0.6	0.1	0.2
Al	2.9	0.1	0.1
Mn	3.4	2.8	0.2
SO4	319.8	362.0	180.0
Sb	BDL	NM	0.005
As	BDL	NM	0.001
Ba	BDL	NM	0.100
Be	BDL	NM	0.005
Cd	BDL	NM	0.005
Cr	BDL	NM	0.050
Pb	BDL	NM	0.010
Hg	BDL	NM	0.000
Se	BDL	NM	0.002
Ag	BDL	NM	0.010
Cu	BDL	NM	0.020
Ni	0.402	NM	0.040
Tl	BDL	NM	0.001
V	BDL	NM	0.100
Zn	0.696	NM	0.012

NM = Not Measured

BDL = Below Detection Limit

Middle Fork of Greens Run Project.

Construction of the Middle Fork site was completed in mid October 2002. The latest sampling event, November 14, 2002, found the water downstream of the pit lake slag check dam to be pH 10.5 with 43 mg/L of alkalinity (Table 3). However, at the time of sampling, the pit lake had just begun discharging into the top of the OLC and alkaline water had not yet reached the sump at the bottom of the OLC. The kisch basin does not appear to be sufficiently neutralizing the acidity of the spoil seep discharge. Therefore, the sump, which receives water from the kisch basin and OLC, continues to discharge net acid water (990 mg/L acidity and pH of 2.6). A limestone check dam downstream of the sump neutralizes an additional 160 mg/L of acidity. However, the final site discharge remains net acidic.

Once the pit lake begins discharging at flows high enough to reach the sump area below, we anticipate complete neutralization of the acid water in the sump. This will restore nearly 2 miles of the Middle Fork of Greens Run and improve water quality in the lower 3 miles of the mainstem of Greens Run and in the lower Cheat River.

Table 3. Early water quality results from the pit lake at the Middle Fork of Greens Run site.

Sampling Station	US Slag Check Dam	DS Slag Check Dam
pH	2.7	10.5
acidity	1087.2	0.0
alkalinity	0.0	43.0
acid-alk	1087.9	-43.0
Mg	23.9	1.3
Ca	63.7	20.4
Fe	255.0	0.1
Al	51.6	0.3
Mn	3.6	BDL
Cond	4170.0	171.0

BDL= Below Detection Limit

Discussion

Field demonstrations using high alkaline steel slag for AMD neutralization indicate its potential success to treat high acid, high flow discharges. In addition, there have been no indications that placing slag directly within acid environments causing significant increases in trace metal content of receiving streams. Data from the McCarty Highwall site indicate that alkalinity generations from slag systems can be extremely high during the initial months of treatment. However, these alkaline levels quickly decrease and reach equilibrium between 15-30 mg/L within the first four months of treatment.

Early results from the Middle Fork of Greens Run site indicate that steel slag fines within the pit lake are generating over 1100 mg/L of alkalinity and producing net alkaline water at the lake discharge. However, water quality from the kisch basin indicate that larger, less pure, slag materials may be less effective in treating high acid, high flow discharges.

Direct treatment of acidic discharges with high alkaline steel slag is a new passive AMD treatment technology. Due to the chemical composition of steel slag, leaching of trace elements may still remain a concern as these systems begin to generate less alkalinity over time. Therefore, discharges from these systems will be closely monitored for trace element content, as well as pH acidity and alkalinity.

Literature Citations

Earle J, and T Callaghan. 1998. Impacts on mine drainage on aquatic life, water uses and man-made structures. Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. 4:1-10.

Kimmel, WG. 1983. The impact of acid mine drainage on the stream ecosystem. *In*: Majundar SJ, Miller WW (Eds). Pennsylvania Coal: Resources, Technology and Utilization. Pennsylvania Academy of Science publication, 424-437.

Skousen, JG. 1995. Acid mine drainage. *Green Lands*. 25(2): 52-55.

Sobek, A, W Schuller, JR Freeman, and RM Smith. 1978. Field and laboratory methods applicable to overburden and minesoil. U.S. EPA, Cincinnati, Ohio, EPA-600/2-78-054, p 203.

United States Steel Corporation. 1964. The Making And Shaping Of Steel. Ch 7, p 216-220.

Ziemkiewicz PK, and JG Skousen. 1998. The use of steel slag in acid mine drainage treatment and control. *In*: Proceedings, 19th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, West Virginia, April 7-8.

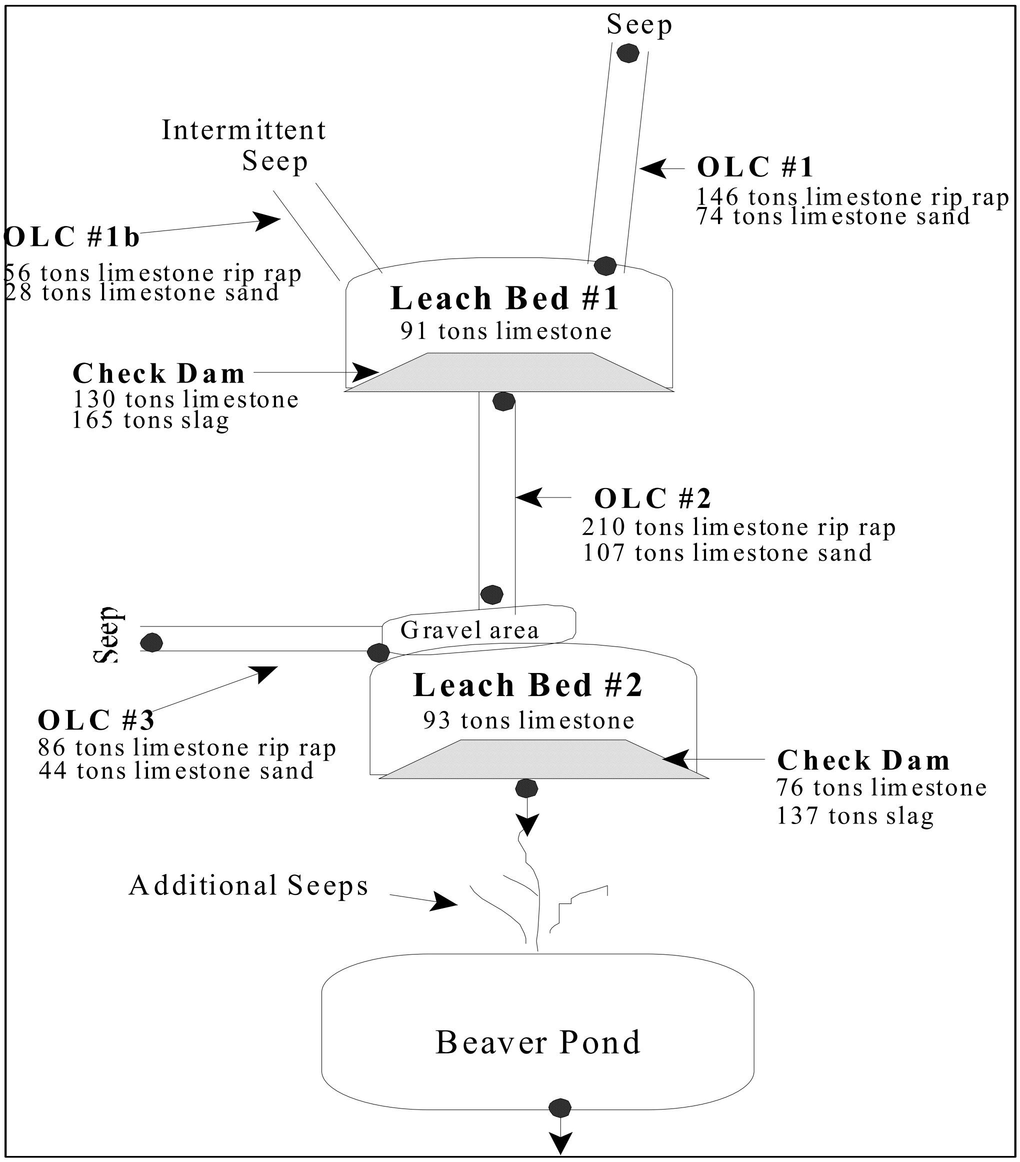

Figure 1. Diagram of McCarty Highwall AMD Treatment System. *Acidic seep water enters the leach beds through three open limestone channels. Treated water exiting the system from leach bed #2 encounters additional acid seeps downstream of the site.*

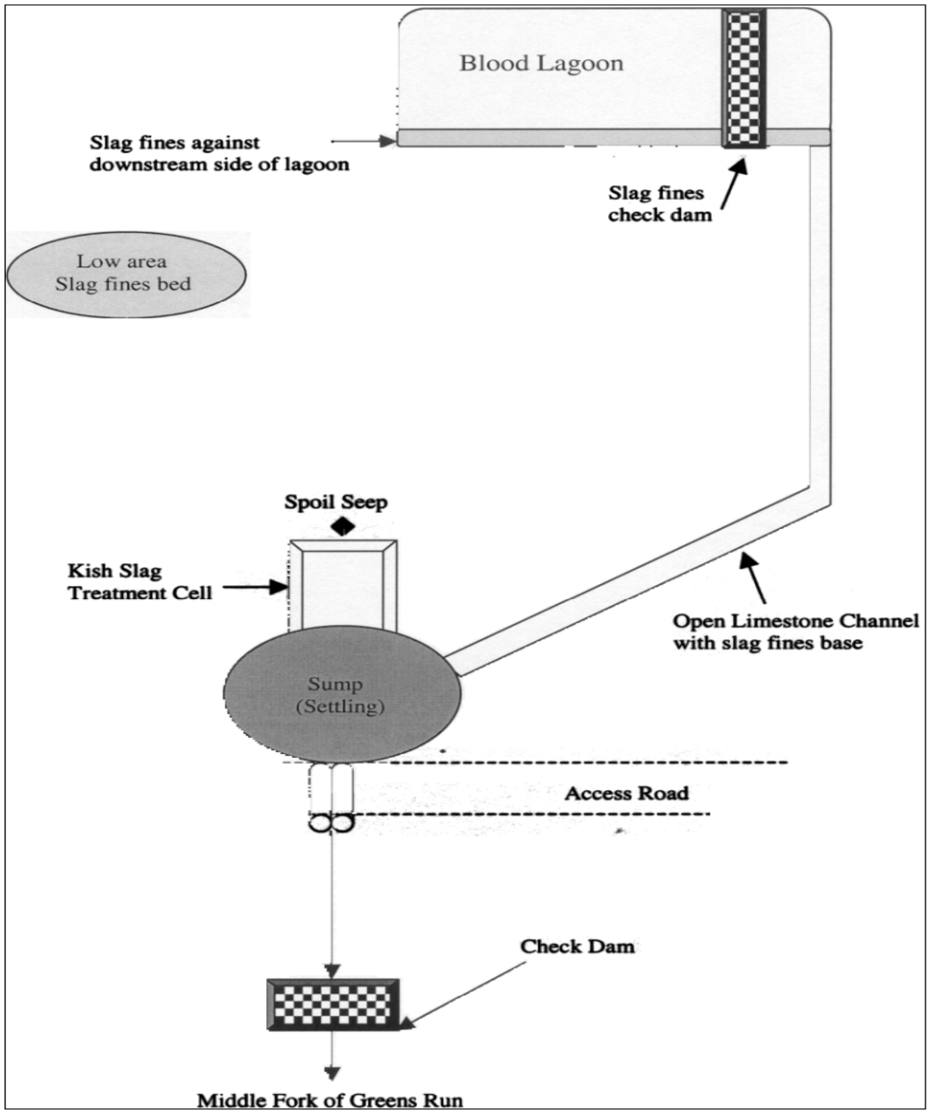

Figure 2. Diagram of the Passive Treatment Systems at the Middle Fork of Greens Run Site. *Acid water enters the system through a seep in the bottom of the pit lake and through a spoil seep at the head of the kisch basin. Acid water is neutralized by steel slag fines, kisch slag and limestone.*

Figure 3. Net Acidicty Concentrations for System Discharge and Downstream of McCarty Highwall. *Discharge occurs at the downstream toe of the second slag leach bed and the beaver pond is located approximately 1/2 downstream of the treatment system.*