THE USE OF STEEL SLAG IN PASSIVE TREATMENT DESIGN FOR AMD DISCHARGE IN THE HUFF RUN WATERSHED RESTORATION¹

James Hamilton, Jim Gue, and Cheryl Socotch²

<u>Abstract:</u> In 1996 the Ohio Department of Natural Resources (ODNR) along with state, local, government agencies, and citizen's group formed the Huff Run Watershed Restoration Partnership, Inc. (HRWRP) to clean up the poor water quality in the Huff Run Watershed. The Lindentree and Lyons passive treatment systems were designed and installed with the use of steel slag to produce several hundred times more alkalinity per equal volume as compared to limestone to help treat the acid mine drainage (AMD) in the watershed due to years of unregulated surface and deep mining.

The Huff Run Watershed is located in Mineral City, Tuscarawas County, Ohio. The primary goals for any of the projects in the Huff Run Watershed are: the reclamation of toxic mine spoil and exposed coal refuse, drain existing acidic impoundments with alkaline treatment of AMD during dewatering and thereby eliminating the main sources of AMD seepages; constructing grass-lined and alkaline rock (limestone riprap and steel slag) channels for collection and diversion of surface water; construction of alkaline rock channels followed by settling ponds and aerobic wetlands as part of the passive treatment system for future AMD seepages; and restoration of the existing central main drainage channel. Both projects encompass 33.6 acres of the watershed and utilized steel slag to supersaturate relatively good water to neutralize low pH waters. Post-construction monitoring for the Lindentree and Lyons projects was conducted in years 2003 and 2005, respectively.

Steel slag is a co-product from the making of steel. The melting process creates an amorphous glassy solid matrix where the oxides are encased in calcium-aluminate-silicates. This glassy matrix is soluble and has a high neutralization capacity for acid mine drainage. Once the steel slag is soluble, the pHs of the dissolved fluids ranges from 10 to 11. Combining these flows with pHs in the ranges of 3 and 4 is showing a net alkalinity going into the Huff Run Watershed. As steel slag does not armor over like limestone, it is expected to provide a long term source of alkalinity.

Site discharges from both the Lindentree and Lyons projects have been net-alkaline, providing a buffer to acidic conditions currently found in the lower reaches of the Huff Run Watershed. The Lindentree, Lyons, and other ODNR projects, should provide a better understanding of the use of steel slag in future AMD remediation projects in the future.

Additional Key Words: Acid mine drainage, alkaline treatment, steel slag,

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² James S. Hamilton, Technical Manager – Aggregate Sales, Tube City IMS, Mercer, PA, 16137. Jim Gue, Environmental Specialist II, ODNR, Division of Mineral Resources Management, Salem, OH 44460,. Cheryl Socotch, Hydrogeologist, ODNR, Division of Mineral Resources Management, New Philadelphia, OH, 44663,

Introduction

Highly acidic mine drainage, or AMD, can be categorized as waters with a pH near 3.5 standard units (SU) and high concentrations of certain metals, such as Fe, Mn, and Al. Generally, neutralization would require a very strong alkaline addition of limestone-based materials, such as that which can be found in steel slags. It is well known that steel slag has high neutralization potential and has shown that it is capable of generating high levels of alkalinity over extended periods of time (Ziemkiewics, Skousen, 1999).

To gain a proper perspective on the use of steel slag in the Huff Run Watershed and other Ohio watersheds, it is appropriate to discuss how it has historically been used in non-mining applications an how it is generated. The use of iron slag in civil engineering dates back to the Roman Empire in the famous Appian Way. Converter slag has been used as an agricultural soil amendment material since the 1880's. Steel slag's physical, chemical and environmental characteristics are subsequently outlined. We will then look at how the elevated pH (above 10) from CaCO₃ precipitate (Tufa) steel making slag creates an environment to effectively treat AMD (Feldmon, 1981). The soluble Ca CO₃ from the steel making slag yields several hundred times more alkalinity than high-quality limestone and can thus serve as a more effective alkalinity supercharger in passive treatment systems (Feldmon, 1981). A steel slag passive treatment system can produce a pH as high as 11 SU; and extend filter bed life, without leaching detrimental metals or metalloids into the surrounding environment. We follow with discussion of steel slag usage with specific AMD remediation projects in the Huff Run Watershed Restoration program. A discussion of other existing projects in Ohio outlining the benefits and drawbacks to using slag is also included. From these projects, alternative methods of applying slag to the passive treatment systems are becoming clear and future work will reflect these observations.

Slag Characteristics

There are three primary types of slag; blast furnace (iron slag), steel furnace (converter), and nonferrous. In 2003 about 19 million tons of slag was consumed domestically. Though each is used extensively in domestic civil engineering, we will focus our attention on steel furnace slag. Steel slag is currently manufactured at around 90 sites in 32 states. Manufacturing of steel furnace slag is done in one of two ways, a Basic Oxygen Furnace (BOF), and an Electric Arc Furnace (EAF). A BOF is normally charged with a 50% hot iron from a blast furnace and 50% scrap charge. Production of an EAF is a 100% scrap charge. Variations in the production of steel are due to the grades of steel required for commercial sale (United States Steel, 1964). These variations in steel production will vary the slags that come from the steel furnaces. Steel slag is a co-product of the making of steel inside a furnace. This means steel slag is created simultaneously inside the BOF and EAF. Table 1 outlines the Typical Chemical Analysis by percentage for the oxides in steel slags. Table 2 outlines the Typical TCLP Analysis by parts per million in steel slags.

Typical Chemical Anaysis (%)		
Calcium oxide	35.41	
Iron oxide	19.24	
Silicon dioxide	14.58	
Magnesium oxide	7.81	
Aluminum oxide	6.93	
Carbon	0.3	
Sulfur	0.21	
Phosphorus	0.18	

Table 1: Typical Chemical Analysis by wt % of oxides in steel slags.

Table 2: Typical TCLP Analysis by parts per million in steel slags.

Typical TCLP Anaysis (PPM)			
Element	steelmaking slag EPA Max.		
Arsenic	< 0.002	5.000	
Barium	1.400	100.000	
Cadmium	< 0.002	1.000	
Chromium	< 0.038	5.000	
Lead	< 0.004	5.000	
Mercury	< 0.000	0.200	
Selenium	< 0.003	1.000	

Steel making slags characteristics vary from furnace to furnace. Similar to natural aggregates, steel furnace slag behavior is largely dependent on its elemental makeup. The steel melting process at 2700° F creates amorphous glassy solid matrices where the oxides are encased in a calcium-alumina-silicate. There are three primary types of steel grade which are high, medium, and low. Each grade is dependent on the C content and steel grades with lower C content are typically of a higher quality. Carbon content is altered by varying the amounts of oxygen, and flux agents (lime and dolime) in the melting process. Flux additions to the furnace lower the melting point and removes S; consequently cleaner steel requires larger flux additions to the furnace. The amount of flux that is added to the furnace directly relates to its propensity to precipitate free lime (CaO). Higher grade steel requires a larger amount of flux which is represented in the final slag having a higher free lime (CaO) content. Lower grade steel requires a smaller amount of flux which will have a lower amount of free lime (CaO) in its chemical makeup.

Steel making slag's elemental makeup consists of Sb, Cd, Cr, Cu, Mn, Mo, Ni, Se, Ag, Ti, Sn V, and Zn (Taylor, 2006). During slag formation in the furnace, many oxides, metals, and metalloids develop to create the final composition. The metals and metalloids in the slag are fused tightly together in complexes of calcium silicates, alumina silicates, and alumina ferrite.

In Austria and Germany soil studies have been monitored for 50 years to determine the effectiveness and heavy metal accumulation in soils from the use of steel slag as an agricultural liming material (Rex, 2006). Toxicity Characteristics Leachate Procedure (TCLP) limits is well within EPA standards. A risk assessment study was run by the Steel Slag Coalition of 63 steel makers and slag processors on 73 different iron furnace and steel furnace slag's in North

America. A "Human Health and Ecological Risk Assessment (HERA)" was run in 1998. The HERA study is based on the worst case exposure assumptions demonstrating that steel making slags pose no meaningful threat to human health or the environment. Slags were demonstrated to be best suited to various residential, agricultural, industrial, and construction applications. The metals and metalloids are not readily available for uptake by humans, animals, or plants, do not bioaccumulate in the food web, and are not expected to bioconcentrate in plant tissue (The Steel Slag Coalition, 1998). Heavy metal leachates are not to be considered a concern due to the tight bond at the calcium-alumina-silicate complex that is formed at 2700° F in a steel making furnace.

The only leachate quality that can be an issue is the elevated pH that results when steel slag comes into contact with water. However, because of leached pH levels of 10 to 11 applications in Acid Mine Drainage abatement engineering can add high levels of alkalinity over long periods of time. Once soluble, the alkalinity levels are present for many years due to the fact that it doesn't absorb CO_2 , which would cause it to revert back to insoluble calcite or armour over (Zeimkeiwicz, 1998). This phenomenon occurs once steel furnace slag is exposure to CO_2 whether submerged in water or exposed to the atmosphere- a white powdery Ca CO_3 (Tufa) precipitate is leached into a surrounding water source (Zeimkeiwicz, Skousen1998). A Tufa precipitate is not only common to steel making slag but also to carboniferous rocks. These natural occurring precipitates in carboniferous rocks have been studied since 1878 (Jones, 1925).

<u>Huff Run</u>

Background

The Huff Run watershed, located in the northeast hills region of Ohio in both Carroll and Tuscarawas counties, has experienced extreme environmental degradation from AMD due to years of unregulated surface and deep mining of both coal and clay that occurred between 1850 through the mid 1950's. Much of the discharge to streamflow is from abandoned deep mines and surface runoff from unreclaimed surface mine refuse. Problems and recommended solutions are defined in the Huff Run Acid Mine Drainage and Treatment (AMDAT) Plan, an Ohio Department of Natural Resources Division of Mineral Resources Management (DMRM) study completed in the year 2000. This plan assessed the impacts of AMD and restoration potential in the watershed. During the study, Huff Run was partitioned into eight (8) stream reaches (Fig. 1). The study identified the lower five reaches of the watershed as being degraded by deposition of sediment and metal oxides and hydroxides. The AMDAT recommended a 'top-down' approach to restoration in the watershed that extends the remediation effort over the greatest length of stream being restored. This has resulted in a restoration philosophy that has emphasized the identification and development of projects in stream reaches 4 and 5. The Lindentree Project, (Site #10 and #43) is located in Reach 5 and is the second project in the AMDAT specified area.

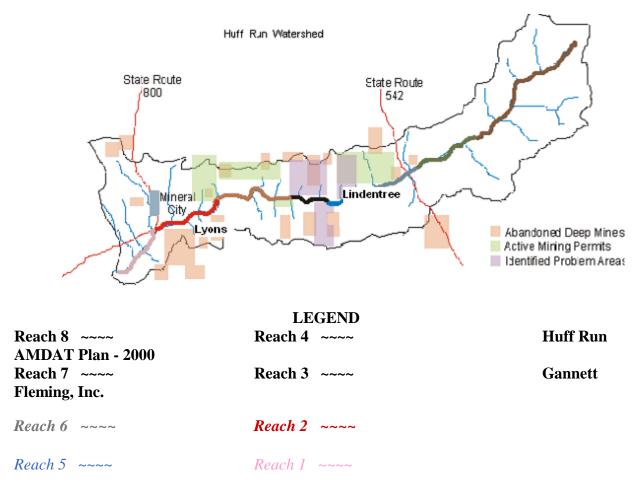


Figure 1: Huff Run Watershed.

The Lyons Project (site #33) exists in lower Reach 2. Huff Run's lower reaches experience seasonal low-flow pH levels between 4 and 5, and the AMDAT defines the need for downstream projects to "buffer episodic low pH excursions". Design of steel slag use for passive treatment was included with this factor in mind. Both Lindentree and *Lyons* used steel slag to supercharge clean water (neutral pH). The projects aid in returning the stream to the Ohio Environmental Protection Agency designated aquatic life classification of warm water habitat. References to the sites can be found in the Huff Run AMDAT Plan: water quality (pages 23 and 24), conceptual design sampling data (Table 1), ranked problems (Table 3) and site map (Fig. 1) (Gannett Fleming, 2000).

Lindentree

AMD source identification, characterization (flow quantity and chemistry), and site topography (site constraints) are the three most important criteria considered on selecting the most appropriate passive treatment measure(s) for AMD discharge, since each passive treatment unit operation has it's own set of limitations with regard to these criteria. The source(s) of AMD seepages and discharge at the Lindentree project site were six separate impoundments found within approximately 90 acres of abandoned, un-reclaimed surface mined areas; these were associated with the Lower and Middle Kittanning coal seams. Except for impoundments

numbers 2 and - 6, the seepages and discharge from other impoundments are slightly to highly acidic with pH varying from 5.88 to as low as 2.99 and the corresponding net acidity varying from 6.5 mg/L to as high as 322.0 mg/L of CaCO_3 equivalent. The highest acidity was from impoundment No. 1. Along with high acidity the discharge from impoundment No. 1 (10 gpm) also contained a very high concentration of Fe (6.94 mg/L), Mn (44.1 mg/L) and Al (21.3 mg/L) compared to the discharges from other impoundments. Impoundments Nos. 2 and 6 have alkaline water with pH 6.64 and 6.28 and net alkalinity of 16.5 mg/L and 6.5 mg/L respectively.

AMD seepages and discharge from all the impoundments at the site flow through varied drainage paths into a main drainage channel leading to Huff Run. Overall AMD flow (25 gpm) to Huff Run from this site as sampled in the main drainage channel had the following characteristics: pH - 3.97, net acidity – 70 mg/L of CaCO₃ equivalent, with total Fe, Mn and Al concentrations of 0.75 mg/L, 18.8 mg/L, and 3.3 mg/L respectively (Socotch, Gue, Seger, Uranowski, 2003). Figure 2 outlines the flow pattern and treatment design of the Lindentree project.

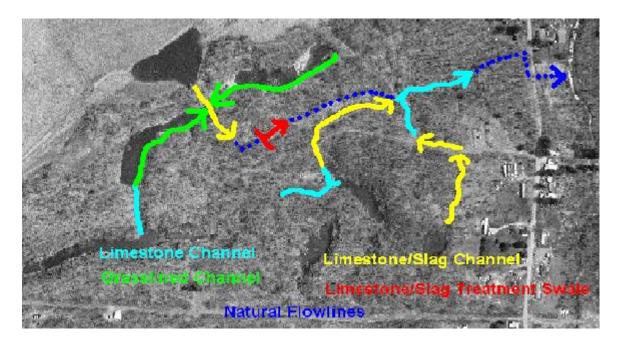


Figure 2: Lindentree flow pattern and treatment design.

To mitigate the AMD discharge problem at this site and to minimize impact on Huff Run, the remediation measures designed are: draining four existing acidic impoundments (#1, #3, #4, and #5) with alkaline treatment of AMD during dewatering and thereby eliminating the main sources of AMD seepages; excavating, backfilling, and grading of the dewatered impoundment areas to provide positive drainage; constructing grass-lined and alkaline rock (limestone riprap and basic steel slag) channels for collection and diversion of surface water; construction of alkaline rock channels followed by settling pond and aerobic wetlands as part of passive treatment system for future AMD seepages; and restoration of the existing central main drainage channel. Steel slag treatment was used in conjunction with clean water (neutral pH). In addition to increasing alkalinity generation by placing steel slag in the open limestone channel (OLC), another design principle of placing steel slag bedding beneath the limestone riprap channels would extend the

service life beyond the normal period of time. It was expected the addition of the steel slag would generate an additional 750 mg/l of alkalinity discharge from the site. Following completion of construction, the sampled discharge from this site falls within these predicted parameters as shown in Table 3 (Chakrovorti, 2004).

Table 3: Passive treatment measures for AMD at this site were designed so that the quality of water discharging into Huff Run is expected to have the following characteristics:

Average Flow	25.0 gpm
pH	7.5 - 8.0 s.u
Total Acidity	0.0 mg/L
Total Alkalinity	80-100 mg/L
Total Iron	0.2 mg/L
Total Manganese	<2.0 mg/L
Total Aluminum	<0.2 mg/L

Lyons

Intensive sampling and analysis of drainage from the project area, now known as the "Lyons" site, was conducted by the ODNR over a twelve-month period beginning in June 1998. Information gathered throughout the watershed was compiled into a document that prioritizes problem areas. As mentioned previously, and according to the Huff Run AMDAT, the Lyons site is the fifth largest source of acid mine drainage pollution in the watershed, discharging more than 335 pounds of acidity and 31 pounds of toxic metals into Huff Run each day. A near total lack of life downstream of the site resulted in an AMDAT recommendation that high priority construction be initiated to eliminate the problems. In 1998, the ODNR hired Gannett-Fleming Environmental Consultants to produce a conceptual design and cost-benefit analysis of the Lyons site, for inclusion with the AMDAT Plan.

In late 2002, the Huff Run Watershed Restoration Partnership Inc., utilizing information from the AMDAT and the Huff Run Watershed Plan, sought and was awarded Ohio EPA funds aimed at eliminating problems from the Lyons site. The ODNR matched the EPA grant, in part, by paying for a detailed project design. This design includes the reclamation of toxic mine spoil and exposed coal refuse, and the installation of alkaline recharge ponds and channels, with the expectation that site discharges will become net-alkaline, providing a buffer to acidic conditions currently found in the lower reaches of Huff Run. ODNR funds and direction led ATC Environmental Consultants to conduct background studies and complete the project design in September of 2004.

The primary purpose of the Lyons Reclamation Project is to reduce the impacts of AMD on Huff Run by reclaiming portions of the exposed toxic mine spoil and coal refuse, establishing positive drainage, and installing passive AMD treatment systems including open limestone channels (OLC's) and alkaline ponds using steel slag. Run-off from the toxic materials was found to increase AMD and sediment loads to Huff Run, especially during rain events and periods of increased flow. In addition two existing impoundments sustained a portion of the acidic base flow from the project area via seepage through coal refuse. The major components of work accomplished with the project include:

- The regrading and resoiling of approximately 161,670 cubic yards of material to fill a large AMD impoundment, elimination of a coal refuse pile located in the central project area and creation of positive patterns to adjacent mine spoils.
- Installation of 2,965 lineal feet of limestone riprap lined drainage channels.
- Installation of 3,115 lineal feet of limestone riprap lined drainage ditches.
- The treatment and dewatering of three existing impoundments.
- Installation of a deep mine drain.
- Placement of 2,070 tons of steel slag ¹/₂" X 0 and 535 tons of steel slag 3" X ¹/₂" in impoundments and channels as a source of alkalinity generation.
- Revegetation of 21 acres of previously barren mine spoils and pits.

The \$665,788.34 in-construction costs were shared by the Ohio EPA (\$340,000.00), ODNR (\$225,788.34) and the US Office of Surface Mining (OSM) (\$100,000.00). Since the project was completed in December of 2005, total project quality discharges for pH have increased from pre-construction levels of 3.1 to 6.3, coupled with greatly reduced quantities of acidity entering Huff Run.

The pH differences are largely attributed to the use of steel slag in the construction of drainage channels and pond bottoms. This relatively new technological demonstration has proved effective at the site, also introducing alkalinity into the adjacent deep mine and boosting its pH discharge from 3.15 to 5.19. The white powdery Ca CO_3 (Tufa) precipitate (1) is leached into the surrounding impoundment from the slag once CO2 reacts with Steel slag. Two impounds located above and hydrologically connected with the deep mine received placements of steel slag berms. This system was designed to spread the supersaturated alkaline Ca CO_3 (Tufa) precipitate throughout the deep mine located directly below so that treatment can occur during high or low levels of precipitation.

As a result the improved quality of discharges from the site have greatly assisted in buffering the low pH of Huff Run's downstream reaches as shown in Table 4, allowing improved conditions for fish and wildlife habitat.

Table 4: Site discharge(s) into Huff Run has shown the following changes pre and post construction.

	Pre-construction	Post-construction
pH	3.10 s.u.	6.33 s.u
Total Acidity	209.40 mg/L	17.7 mg/L
Total Alkalinity	0.0 mg/L	20.1 mg/L
Total Iron	33.8 mg/L	14.1 mg/L
Total Manganese	23.2 mg/L	3.0 mg/L
Total Aluminum	8.7 mg/L	0.0 mg/L

Background of Steel Slag Projects in Ohio

In addition to using steel slag products for AMD remediation projects in the Huff Run watershed, the ODNR, in partnership efforts with a number of other watershed groups

throughout southeast Ohio have seen similar successful remediation efforts with use of the product.

One of the earliest AMD remediation projects in Ohio under the Appalachian Clean Streams Initiative (ACSI) program was completed in 1999 within the Little Raccoon Creek Watershed. The Buckeye Furnace Project, located along Buffer Run in Little Raccoon Creek (Vinton County) included reclamation of over 65 acres of coarse coal refuse and treatment of underground mine discharges and seeps which contributed over 3700 pounds per day of acid to Buffer Run. During early construction, a Permit to Install (PTI) was approved by the OEPA for use of steel slag product at this site. Over 1,750 tons of steel slag was placed in an alkaline recharge system (ARS). Early sampling results from the ARS had pH levels of over 11 and produced over 1,400 mg/l of alkalinity from the leach bed to mix with acidic discharges from the toe of the reclaimed refuse piles. Eventually, alkalinity rates decreased as it was determined that the ARS was undersized based on flow rates and low period of contact time with the steel slag lined (SSL) product. In addition, problems with plugging from high sediment loads upstream from the ARS reduced the effectiveness of the system. Following completion of this project, a Memorandum of Understanding (MOU) was established with ODNR and OEPA for use of the steel slag products for beneficial uses in reclamation projects.

After modifications in design goals to address those inadequacies described above, several other projects were developed with the utilization of steel slag in the Little Raccoon Creek (LRC) Watershed. Reclamation efforts on the Mulga Project (2004) and the Flint Run-Lake Milton Project (2005-2006) used steel slag as a primary product for generating alkalinity. As with the Buckeye Furnace Project, the Mulga Project included reclamation of unreclaimed coal refuse and remediation of underground mine discharges, into Mulga Run, which is a tributary to LRC. This site produced over 750 lbs/day/acid and is the third largest contributor of AMD to LRC. Reclamation efforts included construction of two steel slag leach beds (SSLB) downstream from freshwater sources. Drainage passing through the SSLB exhibited high levels of alkalinity and help to neutralize the downstream AMD inputs. In addition to the SSLB near Mulga Run to allow for precipitation of the metals.

The use of steel slag products in AMD remediation was also used in combination with one or more systems. For example, the Flint Run-Lake Milton project area, located in the headwaters of Flint Run tributary, is the largest contributor of AMD to the LRC watershed. Project goals included a massive 'diversion effort' to reroute surface and subsurface flows around a large coal refuse disposal area, and reclamation of water-filled impoundments and exposed toxic refuse material. Treatment/remediation designs include construction of OLC's with steel slag base, several steel slag leach beds and Successive Alkaline Producing wetland Systems (SAPS).

Other uses of steel slag in AMD remediation in southeast Ohio included a collaboration effort between the Wayne National Forest (USFS) and the Monday Creek Restoration Project (MCRP) watershed coalition with the construction of two SSLB as part of the Snake Hollow Reclamation Project (2004). Several other SSLB and steel slag open-channels are proposed as part of LRC's East Branch Reclamation Project. Designs include steel slag leach beds that are capable of responding to specific seasonal fluctuations.

Summary

The success for the highly alkaline bearing steel slag has been used in Acid Mine Remediation work for 10 years. Most often it has been used to supercharge clean water (neutral pH) to then interact with effluent AMD waters. $CaCO_3$ (Tufa) precipitate is released from steel slag once it reacts with H₂O. This reaction continues until all the free Calcium is used up in the slag.

Steel slag placed above the waters surface has shown great promise as an alkaline material, in drainage channels. However, submerging it appears to provide an even greater treatment option. At the Lyons site the use of steel slag as a pond additive that can charge the deep mine pool has proven to work well. While the use of steel slag and other alkaline products (limestone) help to raise pH and generate high levels of alkalinity, additional measures to allow for precipitation of metals are necessary. A combination of Fe precipitate ponds and wetlands are now recommended downstream from slag beds in order to collect the metals and allow for adequate retention prior to streamflow.

We think to be the most important aspect of steel slag is that it is being produced everyday with continued steel production. Steel slag is a 100% recycled material which helps to support a global mining initiative for sustainability. I am sure that some of the coal extracted from this area was used in the production of steel done years back. It is good to know that a co-product of the modern day steel making process can help to remedy mine seepage which may be part of its legacy.

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