ASSESSMENT OF THE APPLICABILITY OF STEEL SLAG FOR ALKALINE ADDITION TO ACIDIC STREAMS IN SOUTHCENTRAL PENNSYLVANIA[1]

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Abstract. The presence of an existing steel slag material stockpiled from historic steel producing operations located in the Broad Top coalfield region of southcentral Pennsylvania sparked an interest in evaluating the material as an alkaline source which may be an alternative to limestone for remediating Acid Mine Drainage (AMD), which plagues local watersheds. Steel slag from active steel mills is currently used as an alkaline material in AMD treatment. This assessment project involved chemical and physical analyses of the stockpiled steel slag including metals analysis, x-ray diffraction (XRD), Toxicity Characteristic Leaching Procedure (TCLP), and ASTM Extraction. The steel slag material was subject to laboratory and field bench-scale water treatment tests using various water sources. Non-AMD impacted waters, including rainwater and local stream water above AMD impact zones and mildly acidic AMD discharge sources containing low and high dissolved carbon dioxide were tested using the steel slag. In addition to varying the water sources, raw and screened sizes of steel slag were used in container tests to evaluate alkalinity production and the importance of dissolved carbon dioxide. The results of the evaluation indicate that the steel slag has alkalinity-generating capacity due to the presence of calcite ($CaCO_3$) and akermanite ($Ca_2MgSi_2O_7$) minerals identified in the XRD analysis. Additionally, the leaching of potential contaminants in this steel slag was determined to be low based on the results of the TCLP analyses. In all conditions, steel slag increased pH and generated alkalinity within a few hours of contact. The analytical data provided a basis for determining innovative techniques for using the steel slag to add alkalinity within watersheds impacted by AMD.

Additional Key Words: acid mine drainage, passive treatment systems, steel slag, AMD, calcite, akermanite.

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Introduction

Concerned citizens of Broad Top Township and Coaldale Borough in south-central Pennsylvania were determined to find innovative and cost-effective measures to remediate the numerous Acid Mine Drainage (AMD) sites within their 3 watersheds covering 72.5 sq. km. Following a watershed assessment and AMD prioritization, it was determined that nearly all of the 80+ identified AMD discharges will require some form of alkaline addition treatment. Within the 3 watersheds, all of the identified raw AMD sources combined contributed 57 metric tons per year of Fe, 38 metric tons per year of Al, and 492 metric tons per year of acidity.

The desire for watershed restoration resulted in the construction of over two dozen passive treatment systems at AMD sites. All but one of these treatment systems utilizes limestone to generate alkalinity. However, due to the increasing material and hauling costs for these passive treatment systems and the loss of a nearby limestone source, alternatives for AMD remediation were evaluated. Within Broad Top Township and the Six Mile Run watershed (see Fig. 1) are large piles of steel slag located adjacent to historic coke ovens from the former Riddlesburg Steel Mill. Initial estimates indicate that tens of thousands, if not hundreds of thousands, of cu yd of

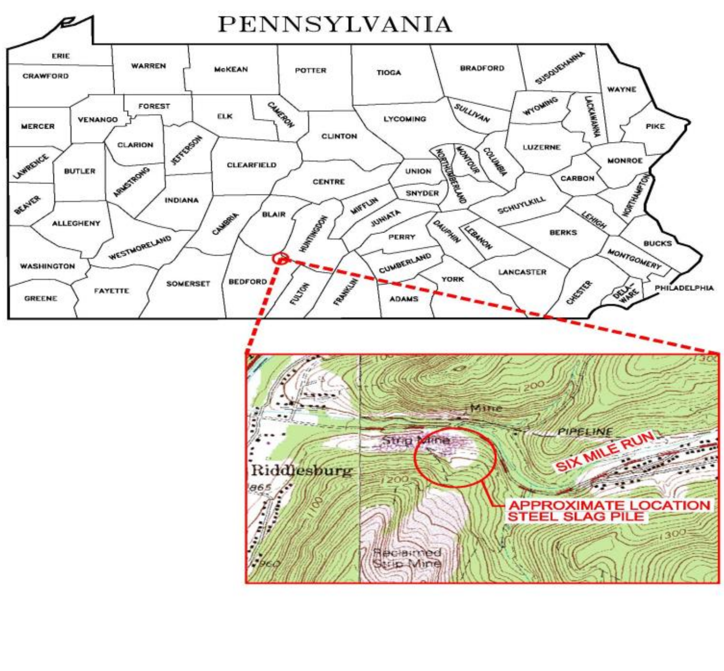

Figure 1. Location Map.

steel slag are available at the site. As a result, Broad Top Township applied to PA DEP Bureau of Abandoned Mine Reclamation (BAMR) for an innovative in-situ/ex-situ treatment technology grant to evaluate the use of the existing steel slag material for water treatment and general alkaline addition capacity. The benefits associated with evaluating the steel slag material located within an acid-impaired watershed present the potential for considerable cost savings from reduced hauling distances and alkaline material costs.

Background

Large piles of steel slag are located within the AMD impacted watershed of Six Mile Run and adjacent to several identified AMD discharges. Literature searches indicate that many steel slag materials are capable of generating high levels of alkalinity within short time periods with several steel slag materials generating 1,500 to 2,000 milligrams per liter (mg/L) of alkalinity (Ziemkiewicz and Skousen, 1998). Depending on steel slag mineralogy, water source chemistry, and treatment system type (open or closed), CO_2 may play a role in alkalinity generation. An open-type system where water and steel slag are contacted and open to the atmosphere would allow any dissolved CO_2 within the water to off-gas and reduce its ability to catalyze the dissolution process. Therefore, this evaluation involved characterizing the steel slag material, conducting laboratory and field tests with different water sources in both open and closed systems, and providing a plan for implementation of the steel slag as an AMD treatment material based on the project results.

It is anticipated that the full-scale use of this steel slag material is plausible for various water source chemistries and flows depending on the treatment approach and objectives. However, use of this material or technology may require bench or pilot-scale testing to verify the applicability to a specific water source compared with current limestone-based approaches. Following completion of the testing, one of the adjacent Six Mile Run AMD discharges could serve as a reasonable test site for implementing a full-scale specially designed treatment system.

The identified tasks for the steel slag evaluation project funded through a grant from PA DEP BAMR were as follows:

- site visit and steel slag sample collection;
- characterization of the steel slag including heavy metal composition, Toxicity Characteristic Leaching Procedure (TCLP) testing, and mineralogy analysis using x-ray diffraction (XRD);
- preliminary testing of steel slag for various water sources;
- laboratory and field bench-scale testing of the steel slag with select water source(s); and
- compilation and analysis of data and creation of a project report.

Materials and Methods

This steel slag evaluation is a preliminary step to determine alkalinity generation rates for specific water sources. Results may enable development and implementation of new innovative treatment technology for alkalinity addition within a watershed based on treatment and restoration goals. The following is a description of the activities by task used to evaluate steel slag as an alternative alkaline material for water treatment.

Task 1 – Site Visits and Sample Collection

Skelly and Loy, Inc. and Broad Top Township personnel visited the steel slag site January 18, 2008, to perform an assessment of the material and determine areas for sampling the steel slag for laboratory analysis and bench-scale testing. On July 18, 2008, Broad Top Township personnel collected two samples of the steel slag; one at the surface and the other roughly one foot below the surface (referred to as subsurface) of the pile. The two samples were collected and placed in containers provided by an independent laboratory and submitted for analysis. Personnel also collected water samples of the adjacent stream and the SX0-D14 AMD discharge for submission to the laboratory for chemical analysis.

Task 2 - Characterization of Heavy Metal Composition, TCLP Testing, and XRD Analysis of the Steel Slag

The specific analyses performed at an independent laboratory on the surface and subsurface steel slag samples are provided as follows:

- ASTM Extraction (ASTM D-3987-85 Method) was used for the analyses below.
  - Alkalinity (endpoints not provided by lab)
  - Chloride

Sulfate

- TCLP Extraction (EPA 1311 Method) was used for the following analyses.

Silver	Chromium
Arsenic	Iron
Barium	Manganese
Calcium	Lead
Cadmium	Selenium

- Neutralization Point and Total Sulfur (PA DER OB ME 861 Method) and Bulk Chemical Analysis (Total Metals by Dry Weight) was used for the analyses below.

Silver	Chromium
Arsenic	Iron
Barium	Manganese
Calcium	Lead
Cadmium	Selenium

- Neutralization Potential (NP) was analyzed by Titration.

In addition, the TCLP extraction was used to determine the leaching of analytes from the steel slag in an acetic acid buffer solution. The analyte concentrations in the extracted solution were used to determine the Toxicity Characteristic (TC) of the material and whether it would be subject to Resource Conservation and Recovery Act (RCRA) disposal regulations. Because of the commonly high heavy metal concentrations within steel slag, the leaching potential from the material was determined from this TCLP analysis for both the raw material and material used in the bench-scale tests.

A sample of the steel slag was also submitted to Activation Laboratories for mineral identification and semi-quantitative analysis using XRD. This type of analysis would provide the type and quantities of minerals found within the steel slag in order to gain an understanding of the alkalinity-producing components of the material.

Task 3 - Preliminary Testing of the Steel Slag and Clean Water Sources

On September 23, 2008, Skelly and Loy personnel visited the steel slag site and collected material using shovels, plastic totes, and buckets for subsequent use in the laboratory bench-scale tests. During this site visit, several liters of stream water adjacent to the steel slag site were also collected. On October 30, 2008, Skelly and Loy personnel sampled additional water sources for use in the preliminary contact tests, which included the RAMP site in the town of Defiance, the headwaters of Longs Run, and the headwaters of Sandy Run. The RAMP site is a wet mine seal discharge that enters the Six Mile Run watershed. Personnel also collected large volumes of rainwater at Skelly and Loy's Harrisburg, Pennsylvania, facility for comparative use in the contact tests because of the convenience and anticipated water chemistry.

Preparation of the steel slag involved creating three size fractions: raw unaltered material (fines up to 10.2-centimeters); 12.7 to 50.8-millimeters (mm); and less than 12.7 mm. Raw steel slag material was crushed as necessary to provide enough material for each size for the bench-scale tests. Finally, batches of each size material were rinsed to remove fines generated during the handling and crushing process and allowed to air dry. Figure 2 shows the sizes used in the tests.

Figure 2. Three different sizes of Judy Hollow steel slag materials used in tests.

The five collected water sources were tested by Skelly and Loy personnel for pH, total alkalinity, and total acidity prior to use in preliminary contact tests in open systems with the raw steel slag to evaluate the alkalinity generation rate and ability to increase pH of the waters in a two-hour testing period. The rainwater, selected as the primary clean water source for the bench-scale testing efforts, was also analyzed by an independent laboratory for pH, total alkalinity, hot acidity, sulfate, total Fe, total Mn, and total Al.

Small plastic tote containers (maximum capacity of 6.1 L) plumbed on one end near the bottom for sampling and draining the water were used for the preliminary contact tests (refer to Fig. 3 for a typical cross section of these containers). Approximately 5.7 L or a 10.2 cm deep layer of the raw steel slag material were placed in test container for the preliminary contact test with the five clean water sources. Measured volumes of each clean water source were added to the raw steel slag in the test container for a two-hour period, and the pH and alkalinity were monitored periodically.

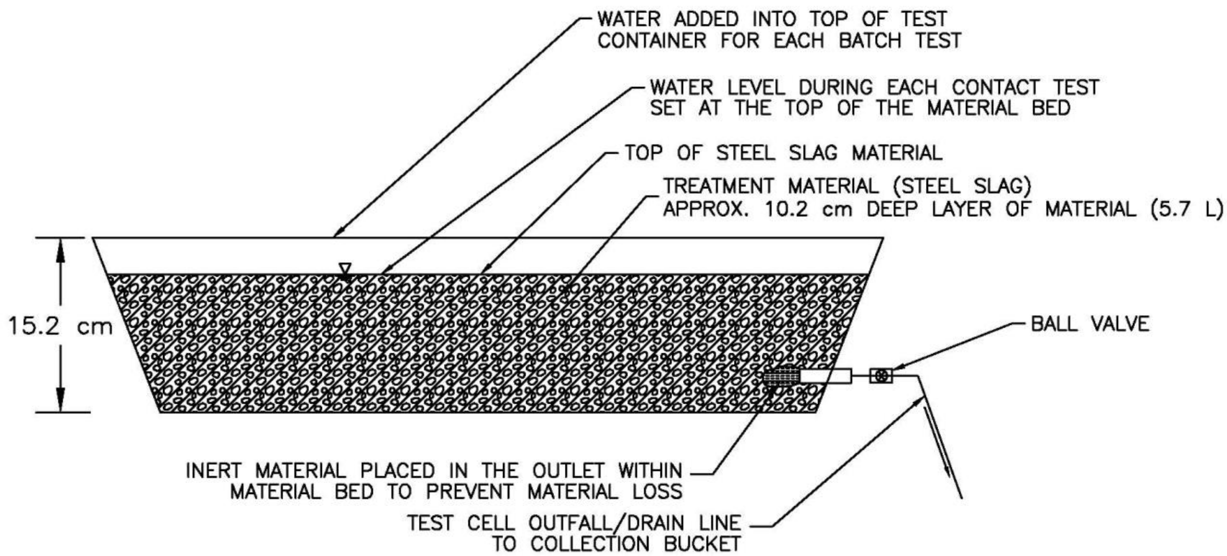

Figure 3. Typical test container cross section used for reactivity/contact tests.

Included with this task were hydraulic conductivity tests for each steel slag size using tap water. The hydraulic conductivity tests were performed by placing approximately 7.6 L (2 gal.) of each size steel slag material in a test column on top of a layer of inert floss material to prevent small slag particles from clogging the outlet opening in the bottom of the column. The test columns (Fig. 4 illustrates a typical cross section of the test column) were 15.2-cm (6-in) clear PVC pipes standing vertically with an open top and a plumbed end cap on the bottom with nylon tubing and a ball-valve connection to control the outflow of water from each column. Water was added to provide 30.5-cm of water over the top of the steel slag material. After measuring the initial water level in each column (the distance from the top of the steel slag material to the water surface), the valve was opened to allow water to flow out of the column. The water level was marked and measured each minute until it dropped below the top of the steel slag.

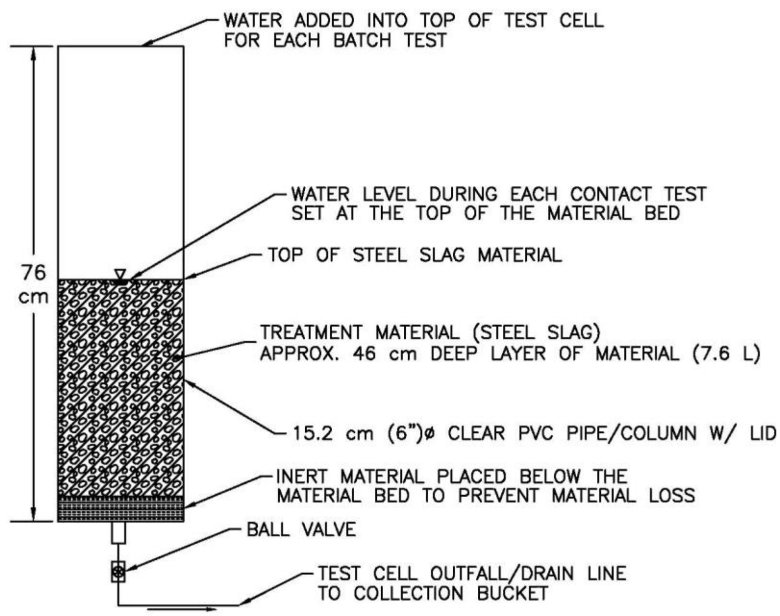

Figure 4. Typical test column cross section used for batch tests.

<u>Task 4 - Laboratory and Field Bench-Scale Tests of the Steel Slag with Selected Water Source(s)</u>

The following four sets of laboratory tests were conducted with both clean and AMD-contaminated water sources for evaluation of the alkalinity generation of the steel slag:

- contact tests using clean water and each size of steel slag in an open-air test container system;
- contact tests using clean water and each size of steel slag in a closed-type container system (not open to the atmosphere);
- batch tests using each size of steel slag in open-air test columns contacted with clean water for 30-minute periods; and
- batch tests using each size of steel slag in open-air test containers contacted with AMD water for 60- and 120-minute periods.

The pH and total alkalinity levels were measured at different time intervals for each of the four test sets using an Oakton® 600 Series Waterproof Meter for pH and temperature and Hach® brand test kits and colorimeter to measure alkalinity, acidity, sulfate, and metals concentrations. The alkalinity was measured as total alkalinity using the Hach® digital titrator kit and titrating to pH endpoints between 3.7 and 5.1, which includes all carbonate, bicarbonate, and hydroxide alkalinity. Total acidity was measured using the Hach® digital titrator kit with the phenolphthalein indicator (pH 8.3) to a colorimetric endpoint. During the one open and two closed system contact tests with clean and AMD waters, pH and total alkalinity were measured after 30, 60, 120, and 240 minutes. In order to roughly mimic a closed system, tests were performed by placing the respective lid on each test container and minimizing head space above the water surface.

The open system batch tests with rainwater were conducted in the test columns containing two gallons of steel slag, with one test column for each size of steel slag. The volume of rainwater added to each test column for the batch tests was measured, with each being filled to just below the top of the steel slag material. Between 1 and 12 of the 30-minute batch tests with rainwater were conducted daily during the testing period. At the end of each 30-minute batch test, the water was drained from the test columns into individual containers for pH measurement. At the end of each day's batch test, total alkalinity was measured. During the 30-minute batch tests with rainwater, samples were collected from the treated water for in-house chemical analysis of pH, total alkalinity, sulfate, total Fe, total Mn, and total Al. An additional set of samples were collected and submitted to an independent laboratory for analyses and included hot acidity.

The open system batch tests with the SX0-D14 AMD were conducted in the test containers with 5.7 L for each steel slag fraction. The volume of AMD added to each test container for a batch test was measured and to a level just below the top of the steel slag material. Between one and six of the 60- or 120-minute batch tests with AMD were conducted daily during the testing period. Similar to the rainwater batch tests, the treated AMD water was drained from the test containers for measuring pH levels. Each test day, total alkalinity was measured. During the 60- or 120-minute batch tests with SX0-D14 AMD water, treated water samples were collected for in-house chemical analysis of pH, total alkalinity, sulfate, total Fe, total Mn, and total Al. Split treated water samples were also collected from each test container for in-house chemical analysis and independent laboratory analysis. Laboratory sample analysis included hot acidity in addition to the in-house chemical analysis parameters.

The final testing of steel slag was performed in the field in May 2009. These field contact tests used raw steel slag material collected during the field visit and two different source waters:

RAMP site water and the SX0-D14 AMD. They were selected because of their difference in chemistry and their proximity to the steel slag source. Open and closed system contact tests were conducted at each water source using an 18.9-L container with a bottom spigot as the open container and a 9.5-L carboy container with a sealable cap and bottom spigot as the closed container both filled with rinsed raw steel slag. The two test waters were collected and poured into each container to just below the top of the steel slag material. The sealable cap was replaced on the carboy container to create a pseudo-closed system with minimal head space above the water surface.

Both pH and total alkalinity were field measured after 0, 30, 60, and 120 minutes of contact time from the RAMP and SX0-D14 tests by collecting a small volume of sample from the spigot of both the open and closed containers. Samples were not filtered before the on-site analyses. An additional 60 minutes contact time was added for the SX0-D14 water in order to achieve an adequate increase in pH levels. Raw and treated water samples following 60 minutes of contact time submitted to an independent laboratory for chemical analyses included the following parameters.

pH	Total Alkalinity
Hot Acidity	Sulfate
Dissolved Silica	Total Aluminum
Dissolved Aluminum	Total Iron
Dissolved Iron	Total Manganese
Dissolved Manganese	Total Sodium
Dissolved Sodium	Total Inorganic Carbon

Only dissolved metals (not total metals) analyses were performed on the closed system samples.

Results

TCLP/ASTM Extractions and Bulk Chemical Analysis

Steel slag samples were collected and submitted to an analytical laboratory for TCLP and ASTM extraction and subsequent leachate analyses, neutralization potential (NP), total sulfur, and bulk chemical analysis. The final pH levels of the TCLP tests were not reported by the laboratory. In addition, a sample of steel slag used for the bench-scale tests in contact with the AMD was submitted for all but the bulk chemical analysis. Table 1 summarizes the results of the analyses on these three samples.

Table 1. Summary of steel slag characterization analyses.

Parameter	Surface Steel Slag	Sub-Surface Steel Slag	AMD Tested Steel Slag
Neutralization Point	8.1	8.2	NOT ANALYZED
Total Sulfur	1.00	1.20	NOT ANALYZED
Silver	<0.65 mg/kg	<0.67 mg/kg	NOT ANALYZED
Arsenic	10.93 mg/kg	7.10 mg/kg	NOT ANALYZED
Barium	273.3 mg/kg	369.8 mg/kg	NOT ANALYZED
Calcium	287,634 mg/kg	320,183 mg/kg	NOT ANALYZED
Cadmium	3.51 mg/kg	0.80 mg/kg	NOT ANALYZED
Chromium	70.2 mg/kg	68.6 mg/kg	NOT ANALYZED
Iron	25,770 mg/kg	5,198 mg/kg	NOT ANALYZED
Manganese	1,692 mg/kg	2,894 mg/kg	NOT ANALYZED
Lead	59.9 mg/kg	772 mg/kg	NOT ANALYZED
Selenium	5.08 mg/kg	8.04 mg/kg	NOT ANALYZED
Alkalinity[1]	120 mg/L	138 mg/L	117 mg/L
Chloride[1]	<2.0 mg/L	<2.0 mg/L	<2.0 mg/L
Sulfate[1]	66 mg/L	119 mg/L	71 mg/L
Silver[2]	<0.005 mg/L	<0.005 mg/L	<0.005 mg/L
Aluminum[2]	<0.05 mg/L	<0.05 mg/L	<0.05 mg/L
Arsenic[2]	0.012 mg/L	0.005 mg/L	0.017 mg/L
Barium[2]	0.69 mg/L	0.56 mg/L	1.56 mg/L
Calcium[2]	1,490 mg/L	1,530 mg/L	1,519 mg/L
Cadmium[2]	<0.002 mg/L	<0.002 mg/L	<0.002 mg/L
Chromium[2]	<0.005 mg/L	<0.005 mg/L	<0.005 mg/L
Iron[2]	<0.05 mg/L	<0.05 mg/L	<0.05 mg/L
Manganese[2]	<0.02 mg/L	<0.02 mg/L	0.15 mg/L
Lead[2]	<0.005 mg/L	<0.005 mg/L	<0.005 mg/L
Selenium[2]	0.027 mg/L	0.04 mg/L	0.022 mg/L

[1] ASTM Extraction Analysis
[2] TCLP Extraction Analysis.

The neutralization potentials (NPs) for the steel slag samples were nearly identical with the surface slag at 39.9% NP (398.8 tons of calcium carbonate equivalents per thousand tons of slag), while the subsurface sample was 39.8% NP. XRD analysis revealed that the steel slag contains three crystalline minerals: calcite; akermanite or gehlenite; and quartz. The semi-quantitative amounts of each compound are summarized in Table 2 as measured by their integrated peak intensities of the strongest peak for each compound.

Table 2. XRD analysis semi-quantitative results.

Identified Mineral	Semi-Quantitative Amount (%)
Calcite $CaCO_3$	41
Akermanite $Ca_2MgSi_2O_7$ or Gehlenite $Ca_2Al(AlSi)O_7$	34
Quartz SiO_2	25

Reactivity/Contact Tests

The five clean water sources were measured in the field for pH and total acidity during water collection for use in the contact tests. Table 3 summarizes the raw pH and total acidity of the five water sources.

Table 3. Raw clean water sources water quality.

Sample	Field pH	Total Acidity (mg/L as $CaCO_3$)
RAMP Site	6.3	47.1
Sandy Run Headwaters	5.1	10.3
Longs Run Headwaters	4.6	13.6
Judy Hollow Stream	7.1	*N.M.
Rainwater	5.1	11

*Hot Acidity was performed by independent laboratory for the sample collected on July 18, 2008, which was -54 mg/L as $CaCO_3$.

Four of the five clean water sources were contacted with the raw steel slag material for a two-hour period and the final pH and total alkalinity were measured to understand the treatment capacity of the slag with different waters in an open system. The Judy Hollow stream water was not tested because the pH was 7.1 with no acidity. Table 4 summarizes the pH and total alkalinity for each of the four water samples in contact with steel slag for two hours.

Table 4. Summary of clean water quality following two hours of contact with steel slag.

Sample	Final pH	Total Alkalinity (mg/L)
RAMP Site	7.6	159
Sandy Run Headwaters	8.2	54
Longs Run Headwaters	8.1	53
Rainwater	8.4	108

Rainwater contact tests were performed using both open and closed systems in the laboratory at ambient room temperature. Tables 5 through 7 summarize the one open and two closed system tests using the rainwater with the three different sizes of steel slag materials.

Table 5. Open system rainwater and steel slag contact tests.

Material	Raw/Unscreened		12.7 - 50.8 mm Screened		< 12.7 mm Screened	
Volume of Water	- - - - 2,500 mL - - - -		- - - - 2,650 mL - - - -		- - - - 2,300 mL - - - -	
Time (Minutes)	pH	Alkalinity (mg/L)	pH	Alkalinity (mg/L)	pH	Alkalinity (mg/L)
0	5.58	18.4	5.58	18.4	5.58	18.4
30	7.90	63.2	8.02	30.4	7.86	124.8
60	8.05	60	8.56	35.6	8.72	134.4
120	8.24	72.8	8.90	42.0	8.73	280.0
240	8.20	80.8	8.96	62.8	8.73	280.0

Table 6. Closed system rainwater and steel slag contact tests (November 26, 2008).

Material	Raw/Unscreened		12.7 - 50.8 mm Screened		< 12.7 mm Screened	
Volume of Water	- - - - 2,500 mL - - - -		- - - - 2,700 mL - - - -		- - - - 2,250 mL - - - -	
Time (Minutes)	pH	Alkalinity (mg/L)	pH	Alkalinity (mg/L)	pH	Alkalinity (mg/L)
0	5.40	19.2	5.40	19.2	5.40	19.2
30	7.58	31.0	8.24	29.0	8.61	64.0
60	8.38	35.0	8.82	26.0	8.73	67.0
120	8.54	48.0	8.98	36.0	8.67	79.0
240	8.55	50.0	9.05	36.0	8.76	91.0

Table 7. Closed system rainwater and steel slag contact tests (December 2, 2008).

Material	Raw/Unscreened		12.7 - 50.8 mm Screened		< 12.7 mm Screened	
Volume of Water	- - - - 2,520 mL - - - -		- - - - 2,430 mL - - - -		- - - - 1,990 mL - - - -	
Time (Minutes)	pH	Alkalinity (mg/L)	pH	Alkalinity (mg/L)	pH	Alkalinity (mg/L)
0	5.63	7.2	5.63	7.2	5.63	7.2
30	8.12	20.8	8.32	16.0	8.58	28.0
60	8.29	24.0	8.60	20.8	8.71	32.4
120	8.62	28.1	8.83	23.2	8.68	37.2
240	8.36	32.8	8.75	40.4	8.61	58.4

The high alkalinity results for the open system with rain water and < 12.7-mm steel slag were most likely a result of the fines entrained in the collected water samples. Both the open and closed system tests indicated that one to two hours of contact time were necessary for rainwater with the steel slag for reasonable alkalinity generation. The results of these contact tests dictated the contact times for the batch test performed in the next phase of the evaluation, which ranged from 60 to 120 minutes.

Contact tests similar to the rainwater tests (including one open and one closed system test) were performed using AMD water in place of the rainwater. Tables 8 and 9 summarize the results of the pH and alkalinity measured levels at the same time frames for the three different steel slag materials in contact with the SX0-D14 AMD. The extremely high alkalinities in the <12.7 mm screened steel slag were most likely a result of entrained fines in the collected water samples.

Table 8. Open system AMD and steel slag contact tests.

Material	Raw/Unscreened		12.7 - 50.8 mm Screened		< 12.7 mm Screened	
Volume of Water	- - - - 2,750 mL - - - -		- - - - 2,640 mL - - - -		- - - - 2,410 mL - - - -	
Time (Minutes)	pH	Alkalinity (mg/L)	pH	Alkalinity (mg/L)	pH	Alkalinity (mg/L)
0	2.95	0	2.95	0	2.95	0
30	5.36	11.1	5.91	27.2	6.87	66.9
60	6.55	45.6	6.48	42.8	7.43	345.2
120	6.78	63.2	6.83	57.6	7.53	208
240	7.02	88.0	7.14	68.0	7.64	199

Table 9. Closed system AMD and steel slag contact tests.

Material	Raw/Unscreened		12.7 - 50.8 mm Screened		< 12.7 mm Screened	
Volume of Water	- - - - 2,560 mL - - - -		- - - - 2,460 mL - - - -		- - - - 2,300 mL - - - -	
Time (Minutes)	pH	Alkalinity (mg/L)	pH	Alkalinity (mg/L)	pH	Alkalinity (mg/L)
0	5.40	19.2	5.40	19.2	5.40	19.2
30	7.58	31.0	8.24	29.0	8.61	64.0
60	8.38	35.0	8.82	26.0	8.73	67.0
120	8.54	48.0	8.98	36.0	8.67	79.0
240	8.55	50.0	9.05	36.0	8.76	91.0

Open and closed system field contact tests were performed on two source waters to better understand the chemistry of dissolved CO_2 and other parameters in the steel slag treatment process. Dissolved CO_2 concentration was estimated by multiplying the total inorganic carbon (TIC) laboratory results reported as milligrams of inorganic carbon per liter by a factor of 3.6. Table 10 summarizes the raw water chemistry of both source waters for the field contact tests.

Table 10. Raw source water chemistry for field contact tests.

Parameter	SX0-D14 AMD	RAMP Site
pH	2.98	6.10
Total Inorganic Carbon	<1.0 mg/L	24.9 mg/L
Total Alkalinity	<10 mg/L as $CaCO_3$	60 mg/L as $CaCO_3$
Hot Acidity	160 mg/L as $CaCO_3$	-50 mg/L as $CaCO_3$
Sulfate	1830 mg/L	56 mg/L
Dissolved Silica	22.0 mg/L	7.8 mg/L
Dissolved Iron	4.74 mg/L	0.39 mg/L
Total Iron	5.00 mg/L	1.23 mg/L
Dissolved Manganese	13.9 mg/L	0.17 mg/L
Total Manganese	14.6 mg/L	0.24 mg/L
Dissolved Magnesium	113 mg/L	7.79 mg/L
Total Magnesium	121 mg/L	9.58 mg/L
Dissolved Aluminum	7.68 mg/L	<0.05 mg/L
Total Aluminum	8.12 mg/L	<0.05 mg/L
Dissolved Calcium	207 mg/L	25.6 mg/L
Total Calcium	219 mg/L	30.9 mg/L
Dissolved Sodium	4.07 mg/L	1.33 mg/L
Total Sodium	4.27 mg/L	1.60 mg/L

The SX0-D14 AMD contained minimal levels of CO_2 (as indicated by the undetectable concentration of TIC), while the RAMP site contained a much higher level of CO_2 (89.6 mg/L as calculated by multiplying the TIC value of 24.9 mg/L by 3.6). Open and closed system contact tests with SX0-D14 and the RAMP site were performed in the field for a total of 120 minutes for the RAMP site and 180 minutes for the SX0-D14 AMD. The pH and alkalinity measurements were performed after 30, 60, 120, and 180 (SX0-D14 only) minutes during the field contact tests. Tables 11 and 12 summarize the pH and alkalinity data collected during the field tests.

Table 11. SX0-D14 and raw steel slag field contact tests - pH and alkalinity data.

	Open System		Closed System	
Volume of Water	- - - - - - - - 8,500 mL - - - - - - - -		- - - - - - - - 7,500 mL - - - - - - - -	
Time (Minutes)	pH	Total Alkalinity (mg/L)	pH	Total Alkalinity (mg/L)
0	2.87	0	2.87	0
30	5.88	29.6	6.36	57.2
60	6.53	*N.M.	7.10	*N.M.
120	6.89	64	7.16	74
180	7.11	74	7.20	76.8

*N.M. = Not Measured (water samples collected and submitted to laboratory for analysis for the 60-minute contact time).

Table 12. RAMP site and raw steel slag field contact tests - pH and alkalinity data.

Volume of Water Time (Minutes)	Open System 7,000 mL pH	Open System 7,000 mL Total Alkalinity (mg/L)	Closed System 5,500 mL pH	Closed System 5,500 mL Total Alkalinity (mg/L)
0	6.32	63.6	6.32	63.6
30	6.78	92.0	6.89	107.6
60	7.10	111.2	7.34	123.2
120	7.43	118.8	7.33	119.2

Water samples were collected from each test container after one hour of contact time during the field tests. The closed system tests were only analyzed for dissolved metals. Table 13 summarizes the results of those chemical analyses from the field contact tests with the steel slag. Figures 5 and 6 graphically illustrate and compare the pH and alkalinity data of the open and closed test containers from the field contacts tests with the SX0-D14 AMD and RAMP site.

Table 13. Water chemistry for SX0-D14 AMD and RAMP site open and closed system field contact tests after 60 minutes.

Parameter	SX0-D14 AMD Open	SX0-D14 AMD Closed	RAMP Site Open	RAMP Site Closed
pH	6.34	7.38	7.15	7.52
Total Inorganic Carbon	12.7 mg/L	17.8 mg/L	29.5 mg/L	31.0 mg/L
Total Alkalinity	50 mg/L*	70 mg/L*	100 mg/L*	120 mg/L*
Hot Acidity	-30 mg/L*	-70 mg/L*	-100 mg/L*	-120 mg/L*
Sulfate	1150 mg/L	1030 mg/L	89.3 mg/L	117 mg/L
Dissolved Silica	22.0 mg/L	30 mg/L	14 mg/L	23 mg/L
Dissolved Iron	<0.01 mg/L	0.28 mg/L	0.01 mg/L	<0.01 mg/L
Total Iron	3.88 mg/L	N.A.	0.92 mg/L	N.A.
Dissolved Manganese	9.62 mg/L	5.69 mg/L	0.52 mg/L	0.41 mg/L
Total Manganese	10.2 mg/L	N.A.	0.70 mg/L	N.A.
Dissolved Magnesium	105 mg/L	80.5 mg/L	10.1 mg/L	12.9 mg/L
Total Magnesium	110 mg/L	N.A.	13.5 mg/L	N.A.
Dissolved Aluminum	<0.05 mg/L	<0.05 mg/L	<0.05 mg/L	<0.05 mg/L
Total Aluminum	4.70 mg/L	N.A.	<0.05 mg/L	N.A.
Dissolved Calcium	310 mg/L	296 mg/L	53.4 mg/L	73.9 mg/L
Total Calcium	325 mg/L	N.A.	70.7 mg/L	N.A.
Dissolved Sodium	4.20 mg/L	3.44 mg/L	1.65 mg/L	1.78 mg/L
Total Sodium	4.53 mg/L	N.A.	2.06 mg/L	N.A.

N.A. = Not Analyzed
* mg/L as $CaCO_3$

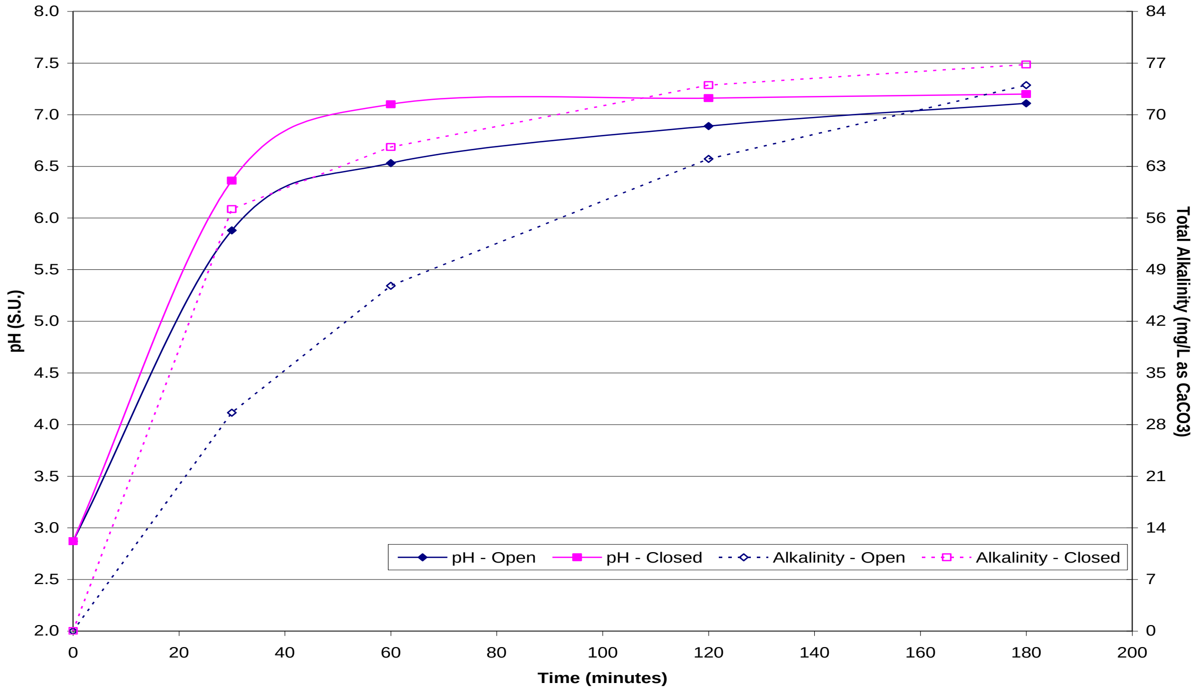

Figure 5. Steel slag field contact tests with low $C0_2$ net acidic AMD: open vs. closed system.

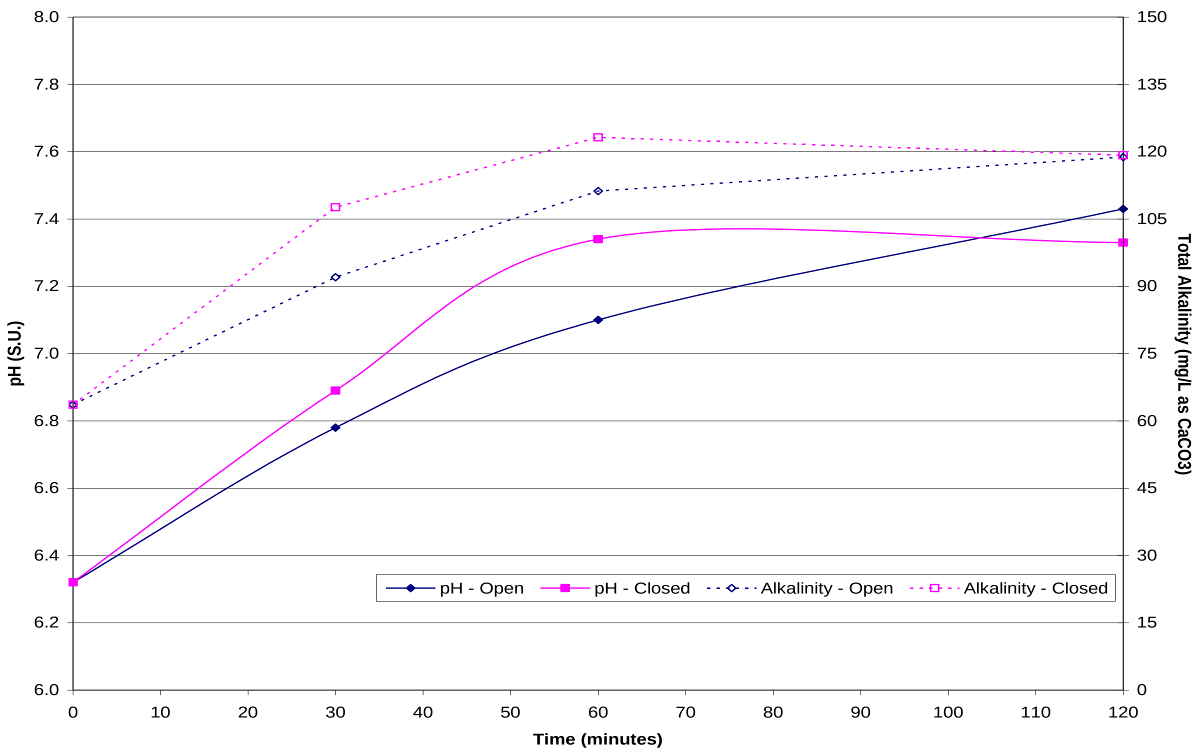

Figure 6. Steel slag field contact tests with high CO_2 net alkaline AMD: open vs. closed system.

Hydraulic Conductivity Tests

The results of the falling head tests performed on the three different sizes of steel slag materials, using tap water to measure the hydraulic conductivity of the material are summarized in Table 14. Because of the coarse sizes of the three different steel slag materials, the hydraulic conductivity was relatively high and similar to limestone commonly used in passive AMD treatment systems.

Table 14. Summary of hydraulic conductivity rates of each size steel slag.

Steel Slag Material Size	Hydraulic Conductivity Rate (cm/sec)
Raw/Unscreened Steel Slag	0.124
12.7 - 50.8 mm Steel Slag	0.139
< 12.7 mm Steel Slag	0.144

Long-Term Alkalinity Production Testing

The first batch tests were performed from November 26 to December 30, 2008, using rainwater in contact for 30 minutes. A total of 130 batch tests were conducted for the long-term batch testing. Treated water total alkalinity was measured on the last batch test each day. The average pH of the raw rainwater used in the batch tests was 5.75 and ranged from 5.06 to 6.57. Table 15 summarizes the data from the 30-minute rainwater batch tests.

Table 15. Summary data for the 30-minute batch tests using rainwater and steel slag.

Size Steel Slag	Avg Vol. of Water Per Batch Test (mL)	Total Vol. of Water After All Batch Tests (mL)	Average Final pH	Average Final Total Alkalinity (mg/L as $CaCO_3$)
Raw/Unscreened	3697	480,580	8.68	28.1
12.7 - 50.8 mm	4392	570,930	8.48	25.1
< 12.7 mm	3210	417,230	9.18	34.7

Laboratory samples of the raw rainwater and treated water from each of the three sizes of steel slag testing columns were collected near the end of the testing period for the 30-minute rainwater batch tests. Table 16 summarizes the water chemistry data from these samples submitted to an independent laboratory.

Table 16. Water chemistry data for 30-minute batch test using rainwater with steel slag.

Parameter	Raw Rainwater	Raw Steel Slag Column	12.7 - 50.8 mm Steel Slag Column	< 12.7 mm Steel Slag Column
pH	6.76	8.42	8.44	8.88
Total Alkalinity (mg/L as $CaCO_3$)	<10.0	14.0	<10.0	10.0
Hot Acidity (mg/L as $CaCO_3$)	2.0	-6.0	-4.0	-8.0
Sulfate (mg/L)	2.3	6.4	5.1	10.2
Total Aluminum (mg/L)	<0.05	0.08	<0.05	0.06
Total Iron (mg/L)	0.03	0.07	0.06	0.06
Total Manganese (mg/L)	<0.01	0.01	<0.01	0.01

Batch tests were then performed from May 12 to June 27, 2009, using vertical standing open top columns of steel slag contacting SX0-D14 AMD for 60 and 120 minutes. A total of 67 batch tests (bed volumes) were performed. The first 24 batch tests with the AMD were performed for 60 minutes, while the remaining 43 batch tests were performed for 120 minutes since the pH of the treated water from the 60-minute batch tests dropped below 6.0 for the larger fraction test columns. The average pH of the raw AMD during the batch testing was 2.98 with a range of 2.67 to 3.16. Tables 17 and 18 summarize the data from the 60- and 120-minute batch tests with the SX0-D14 AMD.

Table 17. Summary data for the 60-minute batch tests – SX0-D14 AMD and steel slag.

Size Steel Slag	Average Volume of Water per Batch Test (mL)	Total Volume of Water After All Batch Tests (mL)	Average Final pH	Average Final Total Alkalinity (mg/L as $CaCO_3$)
Raw/Unscreened	2,538	60,910	6.18	30.8
12.7 - 50.8 mm	2,520	60,470	6.04	20.7
< 12.7 mm	2,231	53,540	6.78	58.9

Table 18. Summary data for the 120-minute batch tests – SX0-D14 AMD and steel slag.

Size Steel Slag	Average Volume of Water per Batch Test (mL)	Total Volume of Water After All Batch Tests (mL)	Average Final pH	Average Final Total Alkalinity (mg/L as $CaCO_3$)
Raw/Unscreened	2106	151,470	6.65	51.3
12.7 - 50.8 mm	2110	151,200	6.61	39.2
< 12.7 mm	2030	140,830	7.01	61.9

On May 19, 2009, during the 15-18th of the 67 60-minute batch tests with the AMD, samples were collected of the raw AMD and treated water from the raw/unscreened steel slag test column. The independent laboratory results of the water chemistry for the 60-minute batch sample are summarized in Table 19.

Table 19. Water chemistry data for 60-minute batch test using SX0-D14 AMD with raw steel slag.

Parameter	Raw SX0-D14 AMD	Raw Steel Slag Column 60-Minute Batch Test
pH	*6.56	6.60
Total Inorganic Carbon	<1.0 mg/L	9.3 mg/L
Total Alkalinity	<10 mg/L as $CaCO_3$	30 mg/L as $CaCO_3$
Hot Acidity	150 mg/L as $CaCO_3$	20 mg/L as $CaCO_3$
Sulfate	1040 mg/L	1060 mg/L
Dissolved Silica	20 mg/L	21 mg/L
Dissolved Iron	3.66 mg/L	<0.01 mg/L
Total Iron	4.58 mg/L	3.14 mg/L
Dissolved Manganese	12.8 mg/L	11.6 mg/L
Total Manganese	15.2 mg/L	13.0 mg/L
Dissolved Magnesium	101 mg/L	103 mg/L
Total Magnesium	123 mg/L	114 mg/L
Dissolved Aluminum	6.89 mg/L	<0.05 mg/L
Total Aluminum	8.47 mg/L	4.50 mg/L
Dissolved Calcium	184 mg/L	249 mg/L
Total Calcium	223 mg/L	273 mg/L
Dissolved Sodium	3.94 mg/L	3.85 mg/L
Total Sodium	4.51 mg/L	4.19 mg/L

*The pH value reported by the laboratory was in question since most of the in-house pH measurements indicated the raw AMD average pH was approximately 3.0.

Discussion

TCLP/ASTM Extractions, Bulk Chemical Analysis, and XRD

The first goal was to characterize the steel slag through TCLP and ASTM extraction, bulk chemical analysis, and XRD. Surface and subsurface samples of the slag revealed some minor differences in chemical composition, which is likely due to weathering of the surface material. The surface steel slag sample contained a higher concentration of iron and lower concentrations of Ca and Mg. RCRA-regulated metals were not readily leached from the steel slag. TCLP leachate metals were below RCRA limits, but sulfate was leached from the material as identified in the ASTM extraction leachate analysis. By way of comparison, steel slag used in the contact and batch tests with the AMD displayed similar leaching potential as the raw material, indicating the material is relatively benign both before and after use in water treatment.

Other evaluation projects for steel slag in AMD treatment have focused on materials with much higher NP than the 40% for the Judy Hollow steel slag used in this evaluation. Ziemkievicz and Skousen (1998) reported NP values ranging from 45% to 75% for several commercially available steel slag sources. Despite the Judy Hollow steel slag's NP and inability to produce over 1,000 mg/L of alkalinity, the reactivity with mildly acidic water is comparable to that of limestone. The XRD mineral identification and semi-quantitative analysis of the Judy Hollow steel slag confirmed the alkalinity-generating characterization of the material, showing that 41% of the material was made up of calcite. In addition, the identified akermanite and/or gehlenite, which are both calcium silicate minerals capable of generating alkalinity, make up an additional 34% of the steel slag. The akermanite is capable of producing six hydroxyl ions (OH^-) for each unit of akermanite dissolved in water (Gao, 1995), similar to treatment with NaOH for increasing pH. Therefore, contrary to the 40% NP result, up to 75% of the steel slag material is capable of generating some form of alkalinity and pH increase from the calcite ($CaCO_3$) or the akermanite/gehlenite (OH^-) minerals. The following is the expected hydrolysis reaction for the akermanite component of the steel slag.

$$Ca_2MgSi_2O_7 \text{ (solid)} + 3H_2O \leftrightarrow 2Ca^{2+} + Mg^{2+} + 6OH^- + 2SiO_2 \text{ (solid)}$$

Reactivity/Contact Tests

Rainwater provided a reliable clean water source with consistent chemistry capable of readily testing steel slag's ability to impart alkalinity without leaching metals. Raw, unscreened steel slag was capable of imparting more than 100 mg/L of alkalinity and an increase in pH to over 8.0 within two hours. Other clean water sources evaluated in the study were also quite reactive but lacked the convenience and consistency of rainwater.

The use of either open or closed test containers resulted in minimal difference in pH and alkalinity. The <12.7-mm steel slag generated the most alkalinity and highest pH values when contacted with the rainwater. The raw, unscreened steel slag produced the second-highest alkalinity and pH values while the 12.7- to 50.8-mm steel slag material produced the lowest alkalinities, likely due to the absence of fines. These contact tests indicated that 30 minutes of contact time with the steel slag materials produced pH levels greater than 8.0 and reasonable alkalinity levels in the rainwater.

AMD laboratory contact tests using SX0-D14 water provided similar results. The starting pH was lower and the acidity higher compared to rainwater. Therefore, a longer contact time was needed for pH and alkalinity levels to reach typical treatment goals. A minimum of two hours (preferably four hours) of contact with the steel slag was determined to consistently increase the pH over 7.0 and generate net alkaline water. As expected, due to source water metal concentrations, metal precipitates were observed. Due to higher acidity and longer contact times, increased dissolution typically resulted in higher alkalinity values. The same trend was observed with the AMD as with the rainwater, where the <12.7-mm steel slag produced the highest alkalinity and pH believed to be due to the presence of fines with much higher surface area.

Field contact tests performed at two different sources of water near the steel slag material to better understand the geochemical processes of the material and the effect of dissolved CO_2 on the alkalinity production. SX0-D14 AMD is characterized as a net-acidic, low CO_2 water source, containing elevated concentrations of Fe and Al. After three hours of contact, no measureable difference in pH and alkalinity was observed between the open and closed systems. The pH and alkalinity levels increased more rapidly in the closed system, but achieved similar levels after three hours. Water chemistry data collected from each test container after one hour of contact time revealed differences between the two regarding TIC, acidity, and metals concentrations. Definitive calcite dissolution was measured due to the increase in Ca concentrations, while a 50% greater increase in TIC and a moderate increase in dissolved silica in the closed system was measured indicating some level of akermanite dissolution.

The second water source for the field contact tests was the RAMP site characterized as net-alkaline and high CO_2 (89.6 mg/L) with low dissolved metals. The RAMP site was also considered as a potential full-scale implementation site for a steel slag treatment system to impart alkalinity directly to Six Mile Run. No significant difference was identified when comparing the open and closed systems. It appears that the dissolved CO_2 is elevated enough to promote dissolution of the steel slag in an open system. Calcium, silica, and sulfate concentrations were increased following contact of the RAMP water indicating both calcite and akermanite dissolution.

Hydraulic Conductivity of the Steel Slag

The smallest steel slag material, <12.7-mm size, yielded the highest hydraulic conductivity. Screening the slag results in more uniform sizes and consistent void space compared to the raw, unscreened material that can vary from several inches in diameter to a fine dust. The <12.7-mm steel slag material had a calculated void space of 42%, the raw slag was 49%, and the 12.7- to 50.8-mm slag measured in at 58%.

Long-Term Alkalinity Production Testing

Since the 130 bed volumes of rainwater did not expend the steel slag, it is difficult to predict the life expectancy of the material with the rainwater. The steel slag effectively treated the rainwater to pH levels ranging from 8.5 to 9.2 on average and generated approximately 30 mg/L of alkalinity, with the highest levels produced by the <½-inch steel slag. The pH levels in the mid to upper 8's indicate that the dissolution of akermanite is likely, which produces hydroxyl alkalinity. Increasing the contact time would be the only means to promoting more alkalinity generation from the steel slag with the rainwater.

The 24 bed volumes or batch tests using the SX0-D14 AMD for 60 minutes did reach a so-called endpoint with final pH levels below 6.0 and net acidic water. Average pH levels of the 60-minute tests ranged from 6.0 to 6.8, with higher pH observed for the <12.7-mm steel slag column. The next 43 bed volumes contacted the steel slag for 120 minutes. The average pH levels of the treated AMD following 120 minutes of contact time with each steel slag was 6.6 to 7.0, again with the higher values occurring in the <12.7-mm steel slag. The alkalinity significantly increased from the 60-minute to the 120-minute contact time for the raw/unscreened and 12.7- to 50.8-mm steel slag, while the <12.7-mm steel slag showed minimal increase in alkalinity (near maximum alkalinity was achieved over a shorter period). The water chemistry data also showed that minimal dissolved silica was added to the AMD after 60 minutes of contact with the steel slag, but the TIC and calcium levels increased moderately. These details indicate that the akermanite dissolution was low while the calcite dissolution was more apparent. The dissolved Fe and Al were significantly removed and retained in the bed. Analyses of the 120-minute batch tests showed alkalinities between 32 and 66 mg/L, metals removal and retention within the steel slag, and neutralization of most (if not all) of the acidity. As expected, the <12.7-mm steel slag produced the highest pH and alkalinity levels, followed by the raw/unscreened and 12.7- to 50.8-mm steel slag materials.

Conclusions

Steel slag material is an abundant and viable source of alkaline addition to certain water sources requiring minimal processing prior to use. Basic excavation, screening, and hauling make it very favorable option to the locally impacted watersheds.

Variations in the steel slag material may exist throughout the extensive piles, but the characterization and water treatment effects of the material used in the study are considered representative of its potential application. Periodic laboratory analysis for NP or mineralogy during excavation would be prudent. The basic characteristics indicate presence of heavy metals with iron and calcium the most abundant. The primary minerals are calcite, akermanite/ gehlenite, and quartz. Finally, the TCLP results indicated limited leaching potential of the steel slag with an NP of about 40%.

The hydraulic conductivity of the steel slag is favorable for use in a treatment system. However, hydraulic conductivity will become compromised in the presence of metals removed from the treated water.

The field contact tests using two chemically different water sources in close proximity to the steel slag pile were the most telling of the project tests. The laboratory contact tests using the rainwater and AMD provided much useful information including criteria for performing the batch tests. However, the data collected as part of the field contact tests provided insight into the geochemistry of the Judy Hollow steel slag and the comparison of an open system versus a closed system. The RAMP site AMD, a high carbon dioxide and net alkaline water source, readily dissolved the alkaline minerals of the steel slag and is considered a highly prospective site for a full scale system to impart alkalinity to the lower segment of Six Mile Run. Approximately two to four hours of contact time were estimated for the steel slag and RAMP site water to reach equilibrium and consistently produce alkalinities over 100 mg/L.

Contacting steel slag with the SX0-D14 AMD showed promise as an alkaline treatment material capable of raising the pH and generating net alkaline water within one to two hours. After one hour of contact with the steel slag in a closed system, the TIC and dissolved silica levels increased, indicating that the acidic water interacts with both the calcite and akermanite in the steel slag. This rapid dissolution of the alkaline minerals treated the AMD from a pH of 3.0 to 7.4 and a net acidity from 160 to -70 mg/L within one hour. Because of the proximity of the

SX0-D14 AMD to the Judy Hollow steel slag pile, a small-scale closed bed of the steel slag material was recommended for further evaluation of the long-term treatment potential. However, clogging potential must be considered and addressed.

The rainwater batch tests with the steel slag provided a basic understanding of the short contact times needed to treat a relatively clean water source. While the generated alkalinity levels were low to moderate, a conceptual application was developed that could be applied to urban areas or large roofed areas where AMD or acid precipitation is a problem. Rain barrels or small plastic tanks filled with steel slag material could be distributed to residences for the purpose of imparting alkalinity into rainwater captured from downspouts and then conveyed into the acid-impacted watersheds at critical locations. The treatment of rainwater would be most effective during small and frequent rainfall events optimizing contact times. Initial calculations assume that a residential roof has an average surface area of 93 square meters and drains to 2 downspouts with each plumbed into a 380-L barrel or tank containing the raw steel slag material with a void space of 50%. Considering this type of system, a one-month rainfall event of 1.4-cm in 30 minutes (Pennsylvania) would have approximately 10 minutes of contact time with the steel slag. The cumulative effect of this type of application using a natural event and the alkalinity-generating capacity of the steel slag material could have significant measureable effects on acid-impacted watersheds.

The results and findings of the Judy Hollow steel slag project provided information that will be useful in future restoration projects within local watersheds. The presence of thousands of tons of alkalinity in an under-utilized waste product located in a watershed still severely impacted by AMD warrants further investigation and small-scale low risk test applications. The benefits to the local community would be substantial, and this unique opportunity deserves attention as a resource recovery, beneficial reuse, and watershed restoration effort.

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