Steel Slag in Acid Mine Drainage Treatment and Control[1]

by

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Abstract: Steel slags are composed of calcium alumino-silicate oxides. Most slags have a sandy texture, but others have a silty texture and give a fine, powdery feel. Neutralization potentials of steel slags range from 45 to 78%, which make them candidates for neutralizing the acidity in acid mine drainage. Analysis of total metal content in Mingo Junction steel slag shows high concentrations of aluminum, chromium, iron, manganese, and titanium. Upon leaching this slag with water, the leachate had a pH of 11.7 and an alkalinity of 1450 mg/L as $CaCO_3$ equivalent. In general, steel slag yielded more alkalinity than equal weights of limestone (500 to 1500 mg/L compared to 60 to 80 mg/L) during leaching studies. Leaching the slag with water and a weak sulfuric acid solution showed that the metals contained in the slag were not readily leachable since these metals were found at low concentrations in the leachate. When different amounts of slag were mixed with an acid-producing coal refuse and then leached with water, pH values of the leachate varied between 3.5 and 7.3. Slightly elevated levels of selenium, nickel, manganese, and possibly iron were found in leachates of refuse/slag mixtures compared to refuse alone. Due to slag's high availability in some areas and low cost, steel slags show potential as an acid-neutralizing material for coal refuse and acid-producing spoils, and for treating acid mine drainage directly. If slag is to be used as an alkaline amendment, it must be added in sufficient quantities to ensure nonacid conditions now and in the future, since under acid conditions some metals may become available. Steel slag can also be used as a liming material for soils. The most promising use for steel slag is as a source of alkalinity to fresh waters that may subsequently encounter acid mine drainage, such as alkaline leach beds or limestone sand applications to headwater streams.

Additional Key Words: alkaline leach beds, chemical treatment, passive treatment systems

Introduction

Slag is defined as the solid material resulting from the interaction of flux and impurities in the smelting and refining of metals. The solid product generally forms a silicate glass-like material, which is primarily nonmetallic. In the power industry, boiler slag is the residue from coal burning which sticks to the walls and pipes of the boiler. This slag is removed from the boiler and pipes through routine maintenance and is a valuable product in the construction industry (sometimes called "black beauty"). Boiler slag should not be confused with bottom ash or fly ash, which are by-products of coal burning, and both are continuously generated and removed during coal combustion. In the base metal industry, slags result from the smelting of various ores of copper, zinc, lead, etc. These metal ore slags can have high concentrations of heavy metals imbedded in the glassy matrix or residing on the solid's surface.

In making steel, iron ore or scrap metal are melted in combination with limestone, dolomite or lime. Pure iron is soft, bends easily under loads and has only limited uses. Adding small amounts of carbon, nickel, manganese and other elements convert the iron into various alloys of steel. There are hundreds of grades of steel, ranging from basic carbon steel to high grade stainless steel, with each having unique properties. In this paper, only the slags from the steel-making process are discussed.

Steel making begins by reducing metal oxides (removing oxygen) in the melt to pure iron metal, while scavenging ions such as aluminum, silicon and

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phosphorus. The latter three elements cause problems in steel making because they cause the steel to become weak, brittle or otherwise difficult to roll into sheets in a predictable way. These elements make it nearly impossible to make anything useful out of iron. Even though iron is much more readily available as a resource, these elemental impurities caused enough problems with iron tools that man began making tools from copper (Bronze Age) after stone tools became obsolete (Stone Age). Fortunately, our ancestors discovered that iron's imperfections could be controlled by adding limestone or dolomite. These calcium compounds complex with aluminum, silicon and phosphorus to form slag. Slag floats to the top of the melt, is poured off and placed in piles for disposal. Slag starts its life at about 2,700 degrees F and cools almost immediately. The slag cools so quickly, in fact, that very few crystals form. Rather, the slag solidifies as an amorphous, glass-like solid ranging from fine sand particles to large blocks, both of which can be extremely hard.

Enormous slag dumps or piles can be found anyplace where steel was made over the past 150 years. Many of these slag piles (containing both nonmetallic slag and wasted steel products) are being processed for use as aggregate in road construction, rail ballast and structural fill. Processing involves crushing and grading the slag. Much of the metallic fraction (the discarded steel products in the pile) is removed with large magnets and sold as steel scrap. All of the resulting nonmetallic grades have applications in construction. The finest fraction (-1/8 in.) is the one of particular interest for acid mine drainage (AMD) treatment. This product is referred to as slag fines. Some slag fines are further refined using the proprietory Recmix process. This process involves further grinding and a hydraulic separation process. The fine grinding and flotation further remove metals, which are imbedded in the glassy matrix.

Previous work at the National Mine Land Reclamation Center has centered on other low cost alkalinity sources like kiln dust and fluidized bed combustion (FBC) ash. Both are effective for AMD control and both are heavily utilized by the industry. In an effort to provide the coal industry with the broadest choice of alkaline materials, we are constantly looking for other low-cost alkaline products which may be available in large supply and located within short haul distances to our mining districts. We have worked with slag fines produced by International Mill Service, Inc. (IMS) and Recmix, a product of Recmix of PA, Inc., and have found both to show positive results for AMD control. The products are very different and have different applications.

Properties of Steel Slag

Steel slags are calcium alumino-silicate oxides. Since they form at the melting point of iron (>2,700 degrees F), most compounds with lower boiling points have been driven off. These compounds contain elements like sulfur, selenium, carbon, cadmium, lead, copper, and mercury. Most of the residuals are encased within a glassy matrix. Fortunately, the matrix is soluble and releases calcium and magnesium oxides, which can drive the pH of the dissolving fluid to 10 or 11. Since slag is a coarse glass, it will maintain high permeability (~ 4.5 x 10^{-2} cm/sec) regardless of how much water has passed through it. The permeability of this material can be reduced if it is compacted or ground up into smaller particles. Recmix, on the other hand is a much finer material and barely lets any water pass through (permeability is ~ 1.0 x 10^{-6} cm/sec). Unlike lime, steel slags do not absorb CO_2 from the air and convert back to relatively insoluble limestone according to the reaction:

$$Ca(OH)_2 + CO_2 \dashrightarrow CaCO_3 + H_2O.$$

This is an extremely important property, since it means slag can be left outside, exposed to the atmosphere for years, and still achieve high levels of alkalinity upon dissolution.

Neutralization potentials (NP) of steel slags range from 45 to 78% (Table 1). Most of the residuals are in the form of aluminosilicates and iron oxides. Table 2 summarizes the chemical compositions of Recmix and a slag from IMS in Mingo Junction, Ohio.

Table 1. Neutralization potential of various steel slags.

Steel Slag Type	Neutralization Potential (%)
C fines; Mingo Jct., OH	78
C fines; Weirton, WV	77
Slag fines ½ X 0; Weirton, WV	76
Fallen slag: Cartech; Reading, PA	71
Fallen slag: Lukens; Coatesville, PA	70
Recmix; Washington, PA	69
Slag fines - 1/8 in.; Mingo Jct., OH	66
EAF: Waylite; Johnstown, PA	59
Slag fines - 1/8 in., Hecate; Ashland, KY	59
Slag fines - 1/8 in., USX; Fairfield, AL	53

Table 2. Total elemental compositions of Recmix and Mingo Junction slag fines.

Element	Recmix	Mingo Jct.
	---------- (mg/kg) -----------	
Al	21,625	29,200
As	6	<3
Ba	130	34
Be	<3	<3
Cd	5	67
C	3,050	4,300
Ca	297,320	501,000
Cr	1,988	1,227
Cu	30	75
Fe	8,327	284,000
Pb	14	84
Mg	57,162	98,000
Mn	9,252	70,000
Hg	0.05	<1
Mo	87	36
Ni	157	12
P	74	8,260
K	325	<100
Sb	<3	<3
Se	5	<3
Si	142,196	85,000
Ag	5	<3
Na	299	125
S	1,805	1,492
Ti	3,285	6,000
Tl	<3	<3
Zn	61	80

Slag Leaching and Analysis

Column leaching studies were performed with various thicknesses of -1/8 inch IMS slag from Mingo Junction, OH. Two-inch diameter columns were filled with slag to thicknesses ranging from 4 to 24 inches. Four times each day, 0.5 L of deionized water was poured through these columns for five days (giving 20 leachings per week). Leachings were not performed on weekends. This leaching procedure occurred over a period of three months. After pouring the water into the columns, leachate was collected and a water sample was taken from the collected leachate. Leachate samples were analyzed for pH, electrical conductivity, alkalinity concentration, and metals. Alkalinities are given as mg/L $CaCO_3$ equivalent.

Water pH of leachate was 11.7 and alkalinity averaged 1,450 mg/L (Table 3). The 12-inch-thick layer of slag produced initial alkalinities of 2,000 mg/L, and these alkalinity concentrations gradually declined as more water was flushed through the system (data not shown). At the lowest points (toward the end of the week after constant leaching), alkalinities of about 100 mg/L were found. The 24-inch-thick layer of slag produed similarly high initial alkalinity concentrations and the decline in alkalinity over time was much slower. Even after 100 L of water had flowed through the 24-inch-thick slag column, the alkalinity was still in the 1,750 mg/L range.

In comparison, crushed limestone leached in a similar way yielded alkalinities near 5 mg/L. In order to reach its maximum alkalinity of 80 mg/L (under open conditions), water had to be in contact with the limestone for about 12 hours.

In general, steel slag yielded more alkalinity than equal weights of limestone (from 500 to 2,000 mg/L compared to 60 to 80 mg/L). Hydrated lime or quicklime will yield similar alkalinities as steel slag for a short period, but these lime products expand when wet, allowing little permeability, and gradually turn into

Table 3. Water quality and metal concentrations of leachate after Mingo Junction steel slag was leached with deionized water.

pH	11.7
Cond. (uS/m)	4780
alkalinity (mg/L)	1450
As (mg/kg)[1]	<0.05
Se	0.05
Ba	0.02
Cd	<0.001
Cr	0.03
Cu	0.058
Pb	0.1
Ni	0.041
Zn	<0.002
V	<0.05
Tl	<0.05
Be	0.0013
Ti	<0.05
Sb	0.08
Mo	0.008
Ag	<0.005
Hg	<0.0003
SO_4	1.6

[1]All element concentrations are in mg/kg.

limestone. In order to be effective in a leaching application, lime products need periodic agitation.

Measurements on the time it took for the water to flow through the columns of slag gave permeability values of 4.5×10^{-2} cm/sec. These permeability values were maintained throughout the leachings, and they are similar to the permeability values of large sand-sized particles and fine gravel. Alkalinity concentrations stayed near 2,000 mg/L for extended periods depending on the thickness of the slag layer.

Heavy Metals in Steel Slag

Since most steel slags contain heavy metals, extensive leaching tests were performed with slags. It is important to remember that all steel slags are not the same; they vary in composition, quality, and fineness. Nonetheless, similar steel-making processes (like basic steel vs. specialty or stainless steels) should produce slags that are comparable. In general, basic steel slags like Mingo Junction have lower concentrations of metals than specialty steel slags that often add other metals for specific purposes. Recmix has even lower concentrations of metal than basic steel slags.

Deionized water was passed through a 2-inch diameter by 24-inch long column of Mingo Junction steel slag fines. The leachate metal concentrations were compared to metal standards for the U.S. Environmental Protection Agency's Toxicity Characteristic Leaching Procedure (TCLP) and to EPA's drinking water standards. The results indicate that the slag did not release any element in quantities higher than TCLP limits (Table 3). As for drinking water standards, other than high pH and alkalinity, only Ni was above the EPA drinking water standard. The Ni concentration in leachate was 41 ug/L versus the drinking water standard of 10 ug/L (Table 3).

The same slag was subjected to a TCLP test, which included extracting metals from the slag with a weak acetic acid leaching solution while being shaken for 18 hours (standard EPA procedures). All of the metals listed under leachate parameters in TCLP were below the maximum allowable limits (Table 4), and most of the metals were below detection using an analytical instrument commonly used for measuring metals in solution (ICP-AES).

Given the amount of alkalinity in steel slag, few metals were expected to be mobilized unless the leaching medium became extremely acid or continued leaching eventually exhausted the alkalinity in the slag material.

Table 4. Metal concentrations in leachates following TCLP testing on Mingo Junction slag fines.

Element	Concentration (mg/kg)
As	BDL[1]
Ba	BDL
Be	BDL
Cd	BDL
Cr total	0.047
Cu	0.017
Pb	0.006
Hg	BDL
Ni	BDL
Sb	BDL
Se	BDL
Ag	BDL
Tl	BDL
V	BDL
Zn	0.012

[1]BDL = Below Detection Limit.

To check the release of metals in an acid situation, an acid-producing coal refuse was amended with 2% and 4% slag for neutralization (these rates represent only one quarter to one half the amount of neutralizing material needed to neutralize the acid that is produced from the refuse). The two slags used in this study, J&L and CarTech, were from specialty steel mills. As expected, most of the columns leached acidic water, except for the 4% CarTech column. In spite of acid conditions, the leachate concentrations were, with only a few exceptions, less than that from the untreated refuse (Table 5). Nickel and manganese, two important elements, both increased in leachates from refuse treated with slag compared to leachate from untreated refuse.

Field Applications Using Steel Slags

The alkaline load achievable from a leach bed of steel slag is determined by the amount of fresh water available to drive the leaching process. It is important to note that slag fines in leach beds will plug if exposed to AMD or sediment. Metals will precipitate within the slag material and cause it to stop transmitting water. Leach beds containing slag fines should be used only in conjunction with fresh (metal-free) water. Slag beds can be constructed to catch runoff without a sediment load or to use direct rainfall. The effluent from the leach beds can be allowed to infiltrate directly into a spoil or refuse pile to achieve in-situ AMD treatment, or the effluent can

Table 5. Leachage quality resulting from the addition of 2% and 4% slag from two sources (J&L and CarTecb). The results are from the fifth leach cycle in an accelerated leaching procedure.

Analyte	Units	Control No Slag	Refuse + 2% J&L Slag	Refuse + 4% J&L Slag	Refuse + 2% CarTech Slag	Refuse + 4% CarTech Slag
pH		2.6	4.0	5.3	3.5	7.3
acidity	(mg/L)	1155	157	24	139	9
alkalinity	(mg/L)	0	0	7	0	25
SO_4	(mg/L)	2080	1551	1424	1650	1413
As	(mg/L)	34	18	31	32	40
Se	(mg/L)	1	5	15	3	30
Ba	(mg/L)	639	21	31	773	28
Ag	(mg/L)	2	11	3	2	2
Cr	(mg/L)	41	5	5	36	3
Ni	(mg/L)	507	1000	283	713	57
Cd	(mg/L)	23	38	6	18	3
Pb	(mg/L)	25	9	13	3	20
Mn	(mg/L)	8	36	22	17	3
Fe	(mg/L)	207	162		216	0
Al	(mg/L)	10	1		6	1

be combined with an AMD source to treat downstream of the spoil. Either application has potential for very low maintenance AMD treatment in either active mining or AML program.

Table 6 indicates expected performance and volume requirements in both limestone and steel slag leach beds for a specific flow of water. The alkaline leach bed (with a steady flow of fresh water) can provide up to 1,800 lbs per day of alkalinity compared to 95 lbs per day with open limestone leach beds (open limestone) and 235 lbs per day with an anoxic limestone leach bed (closed limestone).

Conclusions

Steel slag appears to have a number of applications for AMD control and treatment. In addition to the uses identified so far, future work will evaluate its use as a capping material and as an alkaline amendment.

Until more is understood about the leachability of various slags in acid environments, we do not recommend that steel slags be placed in areas that may become acid. If slag is to be used as an alkaline amendment, we recommend that enough slag is added so that the spoil or refuse cannot turn acid. Both Recmix and slag fines have been used successfully as alkaline amendments to spoils. We recommend that slags be considered as surface amendments to soils, as amendments to slightly acidic spoil and refuse (where the slag will overwhelm the small potential for acid production), and as an alkaline material in freshwater leaching beds. In most locations in the Appalachian coalfields, slag can be obtained very inexpensively. Transportation is the major cost component.

Table 6. Expected performance from leach beds constructed with limestone versus steel slag. Two types of leach beds are presented: those with a steady flow of fresh water (alkaline leach bed) and those driven by precipitation only (dry leach bed).

ALKALINE LEACH BED

	FLOW (gpm)	SIDE LENGTH (feet)	DEPTH (feet)	MATERIAL REQUIRED (tons)	FINAL ALK (mg/L)	LIFE (years)	ALKALINE LOAD (lbs/day)
LIMESTONE							
OPEN	100	135	4	6,160	79	200+	95
CLOSED	100	120	4	4,900	196	100+	235
STEEL SLAG							
OPEN	100	118	4	3,009	1,500	5	1,800

DRY LEACH BED

	AREA (acres)	DEPTH (feet)	FLOW (gpm)	MATERIAL REQUIRED (tons)	COST	FINAL ALK (mg/L)	ALKALINE LOAD (lbs/day)
LIMESTONE	5	1	9.13	16,000	$240,000	20	2.2
STEEL SLAG	5	1	9.13	11,760	$176,400	800	87.6