A METHOD FOR EVALUATING THE RISK OF BACKFILLING COAL MINES WITH COAL COMBUSTION BYPRODUCTS AND STEEL SLAG[1]

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Abstract. Industrial waste by-products, such as coal fly ash and steel slag, are being used increasingly in mine land applications. These wastes may be used in surface or underground applications for the neutralization of acid forming materials, formation of barriers to acid mine drainage formation and transport, subsidence control, pit filling, and soil reconstruction. Many of these applications place wastes in direct contact with acidic materials and/or groundwater. In these situations there may be an increased risk of metal leaching from the wastes into groundwater. Several leaching test have been developed to predict the leaching behavior of these waste materials. The most widely used procedure has been the Toxicity Characteristics Leaching Procedure (TCLP). However, this single leaching procedure may underestimate the long-term leaching behavior of many wastes under acidic conditions. The Mine Water Leaching Procedure (MWLP) was developed especially for these unique conditions. This paper outlines the procedures and benefits of this method and compares the results of 2 industrial wastes by-product MWLPs with TCLPs conducted on the same wastes.

Additional Key Words: Mine reclamation, AMD neutralization

Identification Of Wastes

Coal Combustion By-Products (CCBs)

Production of CCBs. Coal ash is the non-combustible portion of the coal that remains in the boiler or exits the boiler along with flue gas. The majority of U.S. coal ash is produced in pulverized coal boilers. In a dry-bottom pulverized coal boiler, ash particles are formed in suspension. Eighty percent of the ash exits the boiler in the flue gas (fly ash) and is collected by fabric filters, called baghouses, or by electrostatic precipitators. The other 20% of the ash falls to the bottom of the boiler where it is collected as bottom ash.

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During wet-bottom pulverized combustion, approximately 50% of the coal ash forms on the boiler walls. This ash then falls into a water filled tank at the bottom of the boiler where it cools quickly and forms a hard, black, glassy material called boiler slag. The remaining 50% of the ash forms as fly ash and exits the boiler in the flue gas (ACAA, 1998).

Since the passage of the 1970 Clean Air Act and its 1995 revision, several clean coal technologies have been developed to reduce SO_2 air emissions from coal-fired power plants. Removal of sulfur from the flue gas occurs either in the boiler during combustion (fluidized bed combustion, FBC) or following combustion in the flue gas scrubber (flue gas desulfurization, FGD). During fluidized bed combustion coal is pulverized and injected into the boiler along with limestone. The calcium reacts with sulfur to prevent the formation of SO_2 gas. This reaction produces calcium oxide (CaO), calcium sulfate ($CaSO_4$), calcium sulfite ($CaSO_3$) and calcium hydroxide ($Ca(OH)_2$) in addition to the coal ash. The FBC fly ash exits the boiler in the flue gas and is collected by a baghouse or electrostatic precipitator, while the FBC bed ash, or spent bed, is removed from the bottom of the boiler. This process can remove up to 90% of the SO_2. However, due to the large amounts of limestone needed to react with the sulfur ($^1/_3$ to ½ ton limestone per ton of coal), large amounts of CCBs are produced.

Sulfur compounds may also be removed from the flue gas following combustion using flue gas desulfurization (FGD) techniques. FGD systems can be added to any boiler and rely on the injection of Ca compounds into the flue gas stream to remove SO_2. There are three basic types of FGD systems; wet scrubbers, spray drying and lime injection. In a wet scrubber system, fly ash is removed from the flue gas prior to entering the scrubber by baghouses or electrostatic precipitators. Once inside the scrubber the flue gas is subjected to a lime slurry spray. The Ca captures SO_2 from the flue gas and forms calcium sulfate ($CaSO_4$) and calcium sulfite ($CaSO_3$). In this system, FGD residue is formed separately from the fly ash, but may be mixed with fly ash or fixative lime for disposal or post-production use.

In spray drying, lime slurry is sprayed into the flue gas that still contains fly ash. The Ca reacts with the SO_2 to produce $CaSO_3$ and $CaSO_4$. The solids then pass into a baghouse or electrostatic precipitator where it is collected along with the fly ash. Lime injection systems are similar to FBC systems in that the SO_2 capture takes place within the boiler. In these systems, lime is injected into the boiler where it reacts with SO_2 and oxygen to form $CaSO_4$, CaO and

$CaSO_3$. These compounds exit the boiler in the flue gas and are removed along with the fly ash by a baghouse or electrostatic precipitator (ACAA, 1998).

Characteristics of CCBs. Fly ash, bottom ash and boiler slag contain significant quantities of Fe, Ca, K and Na (Punshon et al., 1999). Depending of the chemical composition of the source coal, they may also be enriched with As, B, Mo, S, Se, Sr and varying concentrations of other trace elements.

Fluidized bed combustion units produce strongly alkaline ash. FBC by-products, fly ash and spent bed (bottom ash), contain the same type of minerals but in different proportions. The bottom ash is enriched in anhydrite and lime while the fly ash contains more silicon and iron oxides. FBC ashes contain large amounts of gypsum ($CaSO_4$) and, as much as, 25-30% free lime (Ziemkiewicz and Black, 1999). FGD residue consists primarily of gypsum, CaO, and unreacted lime. These byproducts are higher in Ca and S and lower in Si, Al, Fe and trace elements than fly ash. In the case of spray drying and lime injection, the FGD residue will also contain fly ash. FGD materials resulting from these processes may be enriched in other trace elements present in the fly ash. The most important of these trace elements from an environmental standpoint are As, Ba, B, Cd, Cr, Cu, Pb, Hg, Mo, Ni, Se, Sr, V and Zn. However, the trace element concentration of uncontaminated FGD is low. In fact, boron is the only element that commonly occurs in elevated concentrations in FGD materials (Punshon et al., 1999).

Ironmaking and Steelmaking Slag

Production of Steel Slag. Modern steelmaking occurs by one of two technologies: the basic oxygen furnace (BOF) or the electric arc furnace (EAF). Although both types of furnaces produce molten steel, the input materials needed for its production vary. The input materials for the BOF are iron ore, scrap iron, oxygen and limestone. These types of furnaces are typically used for high tonnage production of carbon steel. In contrast, EAFs use scrap and electricity to generate carbon steels and low tonnage alloy and specialty steels (USEPA 1995).

The first step in the production of steel in the BOF, is the generation of molten iron in a blast furnace. Iron ore, coke and limestone are added to the top of the blast furnace while preheated air enters through the bottom of the furnace. The hot air ignites the coke and it reacts to form carbon monoxide (CO) (Equation 1). This CO then reduces the iron oxide to elemental iron (Equation 2). At the same time, the limestone descends through the furnace and reacts to form CaO and CO_2 (Equation 3). The CaO formed from this reaction is used to remove silicates from the iron (Equation 4) (Rochow 1977).

These processes are expressed in the following equations:

$$\mathrm{2C + O2 \rightarrow 2CO} \tag{1}$$

$$\mathrm{Fe2O3 + 3CO \rightarrow 2Fe + 3CO2} \tag{2}$$

$$\mathrm{CaCO3 \rightarrow CaO + CO2} \tag{3}$$

$$\mathrm{CaO + SiO2 \rightarrow CaSiO3\ (slag)} \tag{4}$$

The $CaSiO_3$ becomes the slag, as well as any remaining silica (SiO_2), alumina (Al_2O_3), magnesia (MgO) or calcia (CaO). The liquid slag floats to the top of the molten iron where it can be poured off periodically (Ricketts 2001).

Molten iron from the blast furnace, along with flux, alloys and scrap can then be added to the BOF for the production of steel. The BOF uses high-purity oxygen injection to generate heat, melt the scrap and oxidize impurities. Slag is produced from the impurities, which are removed from the scrap by a combination of the fluxes and the injected oxygen.

In EAF steelmaking scrap is melted and refined using electric energy generated by graphite electrodes. Scrap, lime and carbon are added to the furnace where an electric arc, produced by the electrodes, penetrates the charge. As the temperature in the furnace increases, the charge begins to melt and oxygen is added for additional heat and to react with impurities in the scrap (Jones, 2001). Oxidation of phosphorous, silicon, manganese, carbon and other materials occurs and a slag containing these oxidized products forms on top of the molten metal (USEPA, 1995).

<u>Characteristics of Slag</u>. Slag is the fused product formed by the action of a flux upon the impurities of an ore (US Steel, 1964). In the steelmaking process, slag is formed during the addition of limestone dolomite or lime to the molten iron ore. These calcium compounds complex with aluminum, silica, phosphorous and other impurities in the ore to form slag. The slag floats to the top of the melt and is poured off into piles for disposal, where it cools almost

immediately. What results is much stronger steel product and a pile of glass-like, calcium alumino-silicate oxides, more commonly called slag.

Since slag is formed at such high temperatures most compounds with lower boiler points have been driven off. Any residuals of these compounds, such as sulfur, selenium, carbon, cadmium, lead, copper and mercury, are typically encased within the slag's glassy matrix. Since the chemical bases of slag consists mostly of lime, magnesia and other basic compounds, leaching of this material results in the liberation of high concentrations of alkalinity to the dissolving fluid. However, the lime in slag, unlike ordinary agricultural lime, is in loose chemical combination with silica, iron and manganese and does not "burn" nor revert to carbonates. This is an extremely important property, since it means slag can be left outside, exposed to the atmosphere, and still achieve high levels of alkalinity upon dissolution.

Blast furnace slag is composed primarily of Si, Al, lime and magnesia (where dolomite is used as a flux). These compounds comprise nearly 95% of the total slag. In addition, the slag also contains small amounts of Mn, Fe and alkali oxides, sulfur compounds and iron (1-2%). The basicity of the slag, a function of the CaO/ SiO_2 ratio, is approximately 1.

Oxidized forms of Si, Mn and P make up the largest portion of BOF slag. It also contains various amounts of Ca silicates and Al, Fe, Ca and Mg oxides. BOF slag has a higher CaO/SiO_2 ratio than blast furnace slag (2.5-4.0) and contains as much as 7% free lime. Compared to blast furnace slag it is much more chemically variable and contains higher percentages of iron.

The composition of EAF slag is highly dependent upon the specific grades of steel scrap, iron-bearing materials and fluxes added to the furnace. In general, they have lower basicities than BOF slags and higher concentrations of FeO and P_2O_5 (AISI, 2001).

Benefical Applications Of Industrial Wastes In Coal Mines

There are several beneficial applications of industrial wastes in mine environments. Strongly alkaline materials such as FBC ash, Class C ash, FGD residue and steel slag can be used to neutralize acid forming materials, such as acidic spoil or coal rejects placed in the backfill. Low permeability wastes, such as fly ash and amended FGD or FBC material, can be used as barriers to AMD formation and transport; either in underground mine workings, surface capping, pavement lining, or isolating acidic material in the backfill. Many wastes may also be used to fill underground mine workings for subsidence control and in pit fillings to reach approximate original contour in surface mines. In addition, many wastes contain significant quantities of plant nutrients and may be used as soil amendments during surface reclamation.

Concerns Regarding Mine Applications Of Industrial Wastes

Whenever industrial waste products are placed in direct contact with acidic conditions there is a concern over their potential to leach toxic levels of metals into groundwater. Trace elements, such as As, Ba, B, Cd, Cr, Cu, Pb, Hg, Mo, Ni, Se, Sr, V and Zn, are of particular concern. Several test procedures have been developed in attempt to predict the leaching behavior of these materials. The most widely used procedure has been the Toxicity Characteristic Leaching Procedure (TCLP), which was designed by the United States Environmental Protection Agency to "determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphasic wastes" (USEPA, 1992). However, this test may only account for fast reactions that take place in short term leaching processes (Yan et al., 2000). The Mine Water Leaching Procedure (MWLP) was developed to determine the long-term leaching potential of inorganic analytes present in industrial wastes when placed in aquatic environments. Of particular, concern is the leaching behavior of these materials when placed in acidic environments associated with mining reclamation or and AMD neutralization.

Mine Water Leaching Procedure

Experimental Objective and Background

The Mine Water Leaching Procedure was developed to determine the long-term leaching behavior of industrial wastes in acidic environments. To date, MWLP has been completed on seven industrial waste products; four steel slags, one fly ash, one bottom ash and one Class F fly ash. This paper contains examples from the sequential leachings of two slags and two fly ashes.

Selection of waste and water

Steel slag used in the MWLP was Electric Arc Furnace slag collected from power plants in the Eastern US. Both were non-metallic and had neutralization potentials of 421 and 628 tons $CaCO_3$ equivalent /thousand tons slag. Acid mine drainage for the slag MWLPs was collected from an underground coal mine in Preston County, WV. This is strongly acidic water that is very high in metals. It is typical of underground coal mine drainage from the Freeport coal seams in Northern WV (Table 1).

Table 1. Water Quality of the Underground Mine Discharge Used in the Steel Slag MWLPs. *Water was collected from the source and stored in the laboratory for use in the MWLP. Concentrations are in mg/L.*

Sample ID	Mine Discharge
pH	2.7
net acidity	613.4
Mg	53.5
Ca	247.4
Fe	90.5
Al	37.7
Mn	1.8
Sb	0.295
As	0.100
Ba	0.020
Be	0.028
Cd	0.015
Cr	0.092
Pb	0.197
Se	0.492
Ag	0.035
Cu	0.657
Ni	0.501
Tl	0.482
Zn	2.035
V	0.061
Hg	BDL

*BDL= Below Detection Limit

Table 2: Water Analysis of Acidic Pit Water Used in the Analysis of Indian Fly Ash. *MWLP was performed on the ash using two acid waters. Concentrations are in mg/L.*

Sample ID	Pit 1	Pit 2
pH	2.8	2.6
net acidity	743.7	2128.0
Mg	24.1	72.4
Ca	93.9	192.6
Fe	39.3	240.3
Al	86.0	181.6
Mn	3.0	10.6
Sb	BDL	BDL
As	BDL	BDL
Ba	0.043	0.028
Be	0.039	0.122
Cd	0.059	0.013
Cr	0.023	0.112
Pb	0.028	0.044
Se	BDL	0.037
Ag	BDL	BDL
Cu	0.047	0.169
Ni	0.973	3.257
Tl	BDL	BDL
Zn	5.730	11.800
V	0.492	0.013
Hg	BDL	BDL

* BDL= Below detection Limit

One of the fly ashes was collected from a power station in North Eastern India. This was a light gray, extremely fine ash with a NP value of 5.2 tons $CaCO_3$ equivalent/1000 tons of ash. Acid mine water from two nearby coal pits was used as the leachant (Table 2).

Class F fly ash was collected from an ash stockpile on a reclaimed surface mine in Monongalia County, WV. Leaching water for this MWLP was collected from an acid seep located on the reclaimed mine site. Table 3 contains a chemical analysis of this water.

Table 3: Water Quality of the Acid Seep Used in the MWLP of Class F Fly Ash.
Concentrations are in mg/L.

Sample ID	Seep 1
pH	3.6
net acidity	3168.7
Mg	743.1
Ca	433.1
Fe	223.1
Al	342.4
Mn	278.7
Sb	BDL
As	BDL
Ba	0.013
Be	0.151
Cd	0.017
Cr	0.022
Pb	BDL
Se	BDL
Ag	BDL
Cu	0.020
Ni	5.289
Tl	BDL
Zn	10.349
V	BDL
B	0.243
Hg	BDL

*BDL= Below Detection Limit

Overview of Experimental Units

Agitation Apparatus. The Synthetic Precipitation Leaching Procedure involves the use of two basic experimental units. Unit one is the agitation apparatus, or rotating platform, which holds up to 12 plastic reaction bottles containing either a mixture of CCB and acid mine drainage (AMD) or steelmaking slag and AMD. The unit's primary feature is a 2'x 4' stainless steel rotating platform. The platform possesses a central, fixed section, which is cut to accommodate half of a 12- 2 Liter cylindrical reaction bottles. Twelve more half-circle units are attached by long screws to the central section to allow the bottles to be tightened into place on the platform.

The platform is connected to an electric motor, which rotates the platform at 30 rpm. The control panel is located atop the metal motor housing. The control panel contains the start, stop, reset and brake release switches for the platform. The panel also includes a timer that enables the platform to rotate continuously for 1 to 24 hours.

Filtration Apparatus. Unit two is a stainless steel pressure filtration apparatus. The unit is composed of a stainless steel, lidded, open-ended cylinder over a stainless mesh filter holder and stainless base. The unit is support by three legs attached to the base, which raise the filtration vessel approximately 1½ ft off the lab bench. The base as well as the stainless lid, are attached to the open-ended cylinder with 1" wing nut bolts. Rubber gaskets seal the unit at points of attachment. A ¼" plastic hose runs from an opening in the lid to the regulator of a nitrogen (N2) gas cylinder.

Overview of Experimental Procedure

The Mine Water Leaching Procedure is identical for all waste products. Therefore, a general outline of the procedure is included in this report.

One hundred grams of < $^1/_8$ inch slag or ash were weighed out using a Triple Beam balance (0.1 g accuracy) and transferred into clean, dry, 2-L plastic reaction bottles (these bottles were selected so that they fit snugly in the agitation apparatus). Two liters of acid water were added to the experimental bottles and 2 Liters of deionized water were added to the Control bottles. The bottles were then sealed with Parafilm and the lids were screwed on to ensure a tight fit. Reaction bottles were arranged evenly on the platform and tightened down using wing nut bolts. "Dummy" bottles of tap water were used when needed to balance out odd numbers of experimental bottles. This ensured that there were always 4,8 or 12 bottles rotating on the platform at all times.

After tightening down all bottles into place on the platform the protective plastic shield was lowered into place over both side (front and back). The timer was reset to 18 hours and the green start button was pressed to start the rotating action. The platform rotated end-over-end for 18 hours at 30 rpm.

Following each 18 hours cycle the contents of each bottle were filtered through a .7 um glass, borosilicate filter using a stainless steel pressure filtration unit at or below 40 psi. A clean, 2 Liter plastic or glass container was placed under the base of the filtration apparatus to collect the filtrate. The contents of either the fly ash + acid mine drainage reaction bottle or the slag + acid mine drainage reaction bottle was poured into the top of the stainless cylinder, which was attached to the stainless filter holder and base. The stainless lid was set in place and tightened down with three stainless wing nut bolts. After closing the release valve, the regulator valve was slowly opened on the N_2 tank to increase the pressure inside the filtration unit. The pressure was slowly increased up to 40 psi until all the liquid was removed from the unit.

Following filtration, the N_2 stream was shut off at the regulator valve and at the main gas cylinder valve. The pressure release valve, which is located on the filtration unit lid, was slowly opened until the air pressure inside the filtration unit equilibrated with that of the outside air. The unit was dissembled from the top down by unscrewing the wing nuts bolts holding the lid and the base to the middle cylinder. The filter cake (filter + solids) was removed and saved for use in the subsequent cycle. The filtration unit was then cleaned with soap and water, rinsed with DI water and reassembled for the next filtration.

Filtrates were collected for laboratory analysis following each agitation cycle into a 2-L bottle under the filtration unit. Five hundred mls of this filtrate was transferred into 2- 250 ml plastic sample bottles. One bottle was sent to an analytical laboratory for pH, acidity and alkalinity determinations. The other bottle was acidified using 1 ml of 1N nitric acid and sent to the lab for metal analysis (Sb, As, B, Ba, Cd, Cr, Pb, Hg, Ag, Cu, Ni, Tl, V, Zn, Mo, Fe, Mn, Al, and B- in the case of CCBs).

Data Analysis and Interpretation

Leachate metal concentrations were compared to raw AMD metal concentrations to determine the effect waste products had on water quality. Leachate metals concentrations could be attributed to four possible sources; metal concentrations of the raw AMD, released metals from dissolution of the waste matrix; remobilized AMD metal sludge and remobilized waste metal sludge (Figure 1).

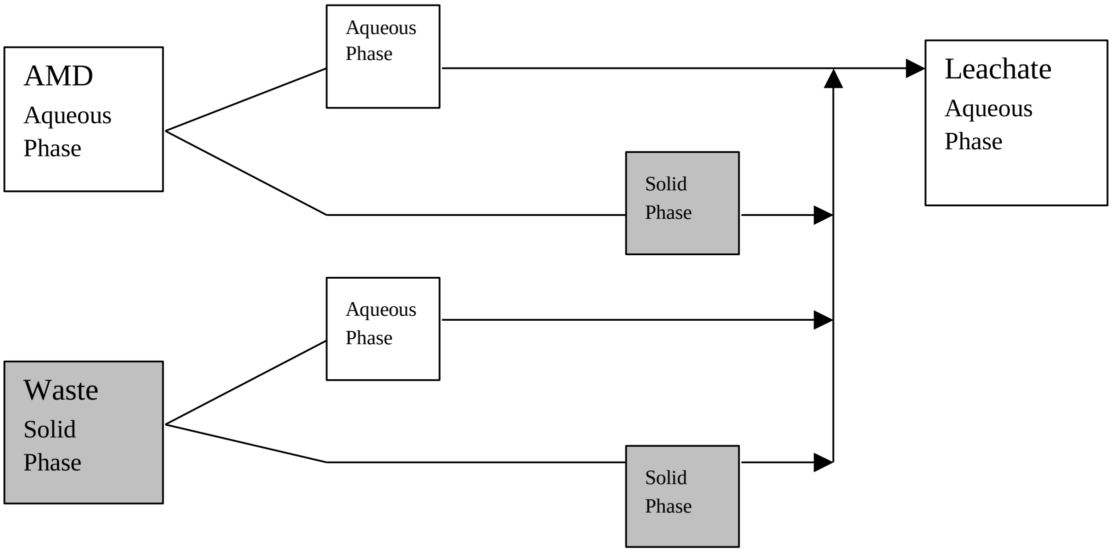

Figure 1. Diagram of the experimental system. *Metals can be imported to the system from either the AMD (aqueous form) or the waste (solid form). Once in the system, metals can either stay in the aqueous phase, precipitate into the solid phase or resolubilize into the aqueous phase.*

It is difficult to identify the source of the metals in each specific leachate. However, by subtracting the metals exported from the system (in the leachate) from the metals imported to the system (in the AMD), it is possible to determine the overall effect that the waste addition has on the concentration of metals in the solid versus aqueous phase. Table 4 is an example of an import/export table that was developed to track to sequestration and release of arsenic during an EAF slag MWLP. Column 1 contains the cycle numbers, 1-60, by multiples of five. Column 2 is a cumulative list of arsenic imported into the experimental system with each new addition of AMD. For example, 2 L of the AMD in this study contained 0.2 mg of As, so by the fifth cycle 0.2 x 5, pr 1.0, mg are arsenic had been added to the system. The export of metals from the system can be tracked by calculating the cumulative amount of metals leaving the system in the leachate. These cumulative values can be used to make inferences about the leaching behavior of individual waste products in acidic aqueous environments. The slag release column of Table 4 is calculated from the difference between the As Out and As In columns. Negative release values represent sequestration of arsenic from the aqueous phase into the solid phase.

Table 4. Example of Arsenic Import/ Export Table for EAF Steel Slag MWLP. *All in, out and release values are cummulative. For example, the value of 1.0 mg for As In at Cycle 5 is the cummulative concentration of As in the import water (AMD) for cycles 1-5. The As Out is calculated similarly. This permits the calculation of the mg of arsenic released into the leachate water as a result of the slag addition to the AMD.*

Cycle	As In mg	As Out mg	Slag Release (mg)	% Released
1	0.2	0.08	-0.12	-60.5%
5	1.0	0.48	-0.52	-51.8%
10	2.0	1.42	-0.58	-28.8%
15	3.0	4.01	1.01	33.5%
20	4.0	11.18	7.18	179.6%
25	5.0	16.50	11.50	229.9%
30	6.0	17.22	11.22	187.0%
35	7.0	17.84	10.84	154.8%
40	8.0	19.23	11.23	140.4%
45	9.0	23.91	14.91	165.7%
50	10.0	28.74	18.74	187.4%
55	11.0	33.50	22.50	204.6%
60	12.0	37.32	25.32	211.0%
average				125.4%

This means that, during this part of the leaching period, more arsenic is entering the system through the AMD than what is exiting the system in the leachate. On the other hand, positive release values indicate arsenic concentrations are higher in the leachate than what can be attributed to the addition of AMD during each cycle. This can be attributed to the release of metals from the waste matrix.

Waste sequestration and release trends can also be shown graphically. Figure 2 contains the import/export trend lines of cadmium for the Pit 1 water/Indian fly ash MWLP. In this graph the import line is above the export line. This indicates a sequestration of Cd from the acid water into the solid phase. The amount of sequestration is equivalent to the area between the two lines. Figure 3 is an example of a metal release trend line for Se from the same fly ash MWLP. Metal release occurs when the export line is above the import line. In some instances, waste product additions have no effect on leachate metal concentrations. In Figure 4 arsenic was present in neither the raw AMD nor the leachate.

The MWLP also enables you to calculate the overall affect of industrial waste additions to mine water and track waste leaching behavior over time. There are five possible trends for metal leaching behavior in the MWLP system; sequestration, release, sequestration then release, release then sequestration, or no effect. Table 5 is an example of a sequestration/release summary table for all metals analyzed in an EAF slag MWLP. The overall effect of waste addition on Sb, Fe, Zn, Be and Cd was sequestration. Barium and vanadium were released throughout the leaching period. Manganese, Cr, As, Tl, Ni, Se, Al, Cu and Pb were all sequestered in the beginning, but began releasing at various points throughout the leaching period. The table shows these points of change, as well as, the pH of the leachates at these points.

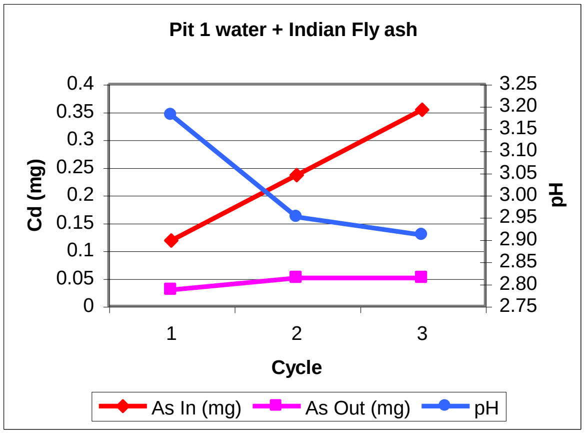

Figure 2. Import/ Export Trend Lines for Cadmium from Indian Fly Ash Leached With Acidic Pit 1 Water for Three Cycles. *In this example, the import line is above the export line indicating sequestration of Cd in the solid phase as a result of the fly ash addition. The area between the two line represents the amount of Cd sequestration in the system.*

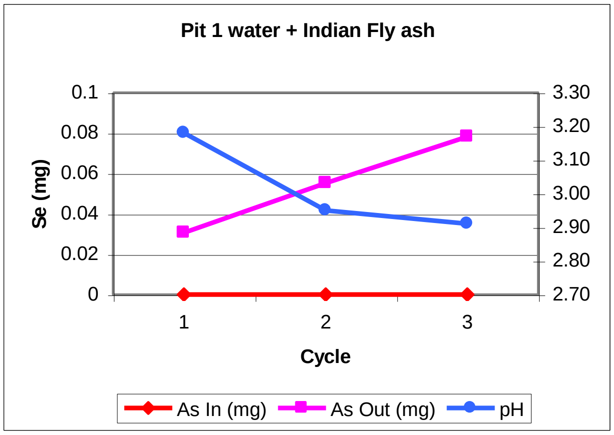

Figure 3. Import/ Export Trend Lines for Selenium from Indian Fly Ash Leached With Acidic Pit 1 Water for Three Cycles. *In this example, the export line is above the import line indicating a release of Se from the solid phase as a result of the fly ash addition. The area between the two line represents the amount of Se release from the system. In this example, where the raw water contained no Se, we can assume that all metal in the leachate is due to fly ash dissolution.*

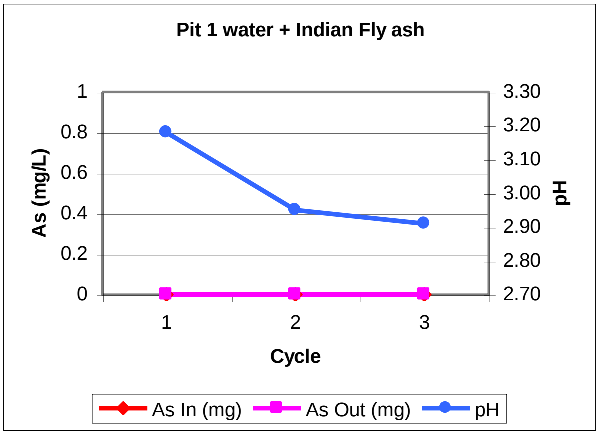

Figure 4. Import/ Export Trend Lines for Arsenic from Indian Fly Ash Leached With Acidic Pit 1 Water for Three Cycles. *In this example, there was no arsenic detected in the raw water or any of the three leachates. Therefore, fly ash addition did not result in any As increases in the leachate.*

Table 5. Example Sequestration and Release Trends Summary Table from EAF Steel Slag MWLP.

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

Comparison of MWLP with TCLP

The objective of the MWLP procedure is to determine the leaching behavior of industrial wastes when placed in acidic mine environments. This procedure differs from the TCLP method in two ways. First, unlike the TCLP, which uses a synthetic extraction fluid, pH adjusted to 2.88 with glacial acetic acid, the MWLP uses acid water from the intended application site. It is intended to more closely simulate field conditions than the typical TCLP method and does not discount the effect of AMD metals on leachate quality.

Tables 6-9 compare elemental concentrations of MWLP and TCLP leachates conducted on two steel slags and two fly ashes. Results from these two tests indicate that the TCLP method may underestimate leaching potential of nearly every trace metal in the analysis.

Table 6. Comparison of Steel slag #1 TCLP and MWLP results for leachate composition. *MWLP allows you to track changes in metal concentrations in the AMD/ slag leachates. TCLP metal concentrations in bold MWLP concentrations throughout the MWLP leaching period. Concentrations are in mg/L.*

Steel slag #1	TCLP analysis	MWLP Raw Water analysis	MWLP Cycle 1 analysis	MWLP Cycle 10 analysis	MWLP Cycle 20 analysis	MWLP Cycle 30 analysis	MWLP Cycle 40 analysis	MWLP Cycle 50 analysis	MWLP Cycle 60 analysis
pH	7.5	2.7	10.5	5.9	4.3	4.2	3.9	3.1	2.8
acidity	0.0	613.4	0.0	69.6	159.1	382.0	498.0	487.5	652.1
est. acidity	106.3	553.4	0.0	145.8	207.5	364.8	435.8	414.9	582.1
alkalinity	2920.9	0.0	64.8	39.4	0.0	0.0	0.0	0.0	0.0
acid-alk	-2920.9	613.4	-64.8	30.2	159.1	382.0	498.0	487.5	652.1
Mg	239.5	53.5	2.9	2.5	79.6	65.9	52.5	45.5	58.1
Ca	2388.0	247.4	822.2	511.0	311.8	328.0	269.0	241.0	236.5
Fe	1.9	90.5	0.3	24.3	12.1	0.7	0.1	7.7	50.0
Al	0.6	37.7	1.0	5.1	19.0	56.3	72.9	60.7	63.7
Mn	**53.6**	1.8	BDL	28.5	36.7	25.5	13.0	9.4	9.8
Sb	BDL	0.295	0.034	0.215	0.239	0.261	0.247	0.259	BDL
As	BDL	0.100	0.040	0.139	0.645	0.063	0.463	0.476	BDL
Ba	**0.790**	0.020	0.166	0.053	0.039	0.047	0.040	0.036	0.030
Be	BDL	0.028	0.005	BDL	0.023	0.028	0.025	0.022	0.020
Cd	BDL	0.015	BDL	BDL	0.009	0.010	0.010	0.010	BDL
Cr	BDL	0.092	0.082	0.083	0.082	0.098	0.105	0.223	0.477
Pb	BDL	0.197	0.042	0.129	0.161	0.209	0.253	0.404	0.226
Hg	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se	0.013	0.492	0.060	0.418	0.504	1.277	1.398	1.367	0.007
Ag	BDL	0.035	0.015	0.055	0.094	0.134	0.394	0.559	0.074
Cu	BDL	0.657	0.240	0.113	0.522	0.683	1.645	1.259	1.172
Ni	0.358	0.501	0.088	0.607	0.576	0.496	0.550	0.377	0.481
Tl	BDL	0.482	BDL	0.596	0.961	0.468	0.494	0.561	BDL
V	0.030	0.061	0.162	0.006	0.044	0.068	0.078	0.039	0.079
Zn	0.121	2.035	BDL	0.993	2.069	1.860	2.683	1.672	2.269

*BDL= Below Detection Limit

This may not be evident from the results of initial MWLP leachates. For example, MWLP leachates sampled early in the Mingo Cool Springs MWLP contain lower thallium concentrations than the TCLP leachates. However, as the leaching period progressed and more acidic water was added to the system nickel concentrations peaked in cycle 30. This increase in nickel could come from two sources: resolubilization of AMD metals or dissolution of the slag matrix. In either case, the single cycle TCLP method would not be expected to predict this trend.

In many cases, leachate concentrations are low in the early stages of the MWLP and then peak at various points in the leaching cycle as the pH of the leaching fluid begins to drop. This is most evident in the high alkaline EAF slag in Tables 6 and 7.

Table 7. Comparison of Steel slag #2 TCLP and MWLP results for leachate composition. *MWLP allows you to track changes in metal concentrations in the AMD/ slag leachates. TCLP metal concentrations in bold exceed MWLP concentrations throughout the MWLP leaching period. Concentrations are in mg/L.*

Steel slag #2	TCLP analysis	MWLP Raw Water analysis	MWLP Cycle 1 analysis	MWLP Cycle 10 analysis	MWLP Cycle 20 analysis	MWLP Cycle 30 analysis	MWLP Cycle 40 analysis	MWLP Cycle 50 analysis	MWLP Cycle 60 analysis
pH	11.8	2.7	12.0	10.3	8.6	7.3	4.1	3.8	3.6
acidity	0.0	613.4	0.0	0.0	0.0	94.8	467.0	444.5	457.1
est. acidity	0.0	550.4	0.0	0.0	5.1	108.7	423.6	387.0	433.6
alkalinity	3899.0	0.0	1524.5	48.1	61.2	19.3	0.0	0.0	0.0
acid-alk	-3899.0	613.4	-1524.5	-48.1	-61.2	75.6	467.0	444.5	457.1
Mg	0.8	53.5	0.4	83.1	125.7	112.0	60.9	51.2	66.4
Ca	4262.0	247.4	1431.5	737.8	429.1	331.5	260.5	271.0	284.1
Fe	0.5	90.5	0.2	BDL	0.0	0.3	0.1	0.3	1.4
Al	0.6	37.2	0.6	BDL	0.8	0.6	72.6	65.5	72.0
Mn	BDL	1.8	BDL	BDL	0.4	57.4	8.9	8.1	9.7
Sb	BDL	0.295	0.038	0.032	0.180	0.205	0.256	0.250	BDL
As	BDL	0.100	0.053	0.068	0.663	0.082	0.476	0.470	BDL
Ba	**0.125**	0.020	0.057	BDL	0.007	0.067	0.030	0.030	0.022
Be	BDL	0.028	0.007	BDL	BDL	BDL	0.039	0.025	0.028
Cd	BDL	0.015	BDL	BDL	BDL	0.008	0.011	0.010	BDL
Cr	0.014	0.092	0.066	0.035	0.055	0.157	0.082	0.083	0.080
Pb	BDL	0.197	0.061	0.042	0.092	0.145	0.157	0.168	0.025
Hg	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se	0.017	0.492	0.056	0.045	0.409	1.435	1.376	1.306	0.007
Ag	BDL	0.035	0.047	0.023	0.116	0.264	0.337	0.506	0.072
Cu	BDL	0.657	0.221	0.017	0.055	0.221	1.030	1.475	1.868
Ni	0.169	0.501	0.091	0.043	0.057	1.242	0.651	0.593	0.692
Tl	BDL	0.482	BDL	0.073	0.837	0.572	0.531	0.504	BDL
V	BDL	0.061	0.083	0.017	0.087	0.128	0.064	0.047	0.066
Zn	0.020	2.035	BDL	BDL	BDL	0.637	3.779	2.306	2.661

*BDL= Below Detection Limit

In the case of the steel slag leachings, barium was the only metal that was higher in the TCLP leachates than in any of the MWLP leachates (cycles 1-60). This was also the case for the Indian fly ash/ AMD 1 MWLP. However, the Indian fly ash/ Pit 1 TCLP leachate also contained increased concentrations of arsenic and selenium compared to the MWLP leachates. The Class F fly ash TCLP leachtae contained higher concentrations of As, B, Ba, Cr and V.

Discussion

Results of the slag and fly ash MWLPs indicate that many industrial waste products can be safely used in mine reclamation and water treatment applications. Import/ export calculations performed on one slag MWLP leachates show that most metals entering the leaching system are sequestered into the solid phase due to the presence of the waste.

Table 8. Comparison of Class F Fly ash TCLP and MWLP results for leachate composition. *MWLP allows you to track changes in metal concentrations in the AMD/ slag leachates. TCLP metal concentrations in bold exceed MWLP concentrations throughout the MWLP leaching period. Concentrations are in mg/L.*

Fly ash #1	TCLP analysis	MWLP Raw Water analysis	MWLP Cycle 1 analysis	MWLP Cycle 2 analysis	MWLP Cycle 3 analysis	MWLP Cycle 4 analysis	MWLP Cycle 5 analysis
pH	4.1	3.6	4.2	3.8	3.5	3.0	2.9
acidity	4320.0	3168.7	2182.7	2906.3	3074.8	2691.8	2772.2
est. acidity	221.3	3023.4	2502.2	3483.3	3215.1	3339.4	3245.3
alkalinity	0.0	0.0	0.0	0.0	0.0	0.0	0.0
acid-alk	4320.0	3168.7	2182.7	2906.3	3074.8	2691.8	2772.2
Mg	15.3	743.1	915.6	996.0	914.6	888.0	880.9
Ca	443.7	433.1	742.6	695.3	694.4	604.2	602.2
Fe	0.7	223.1	6.8	7.6	12.3	46.4	59.2
Al	38.5	342.4	334.2	490.0	451.4	454.6	429.9
Mn	0.8	278.3	342.1	401.7	361.6	348.4	349.4
Sb	0.015	BDL	BDL	BDL	BDL	BDL	BDL
As	**0.135**	BDL	0.022	0.021	0.025	0.020	0.016
B	**6.460**	0.243	4.710	0.850	0.660	0.530	0.510
Ba	**0.128**	0.013	0.076	0.062	0.079	0.061	0.059
Be	0.012	0.151	0.161	0.166	0.173	0.179	0.174
Cd	BDL	0.017	0.023	0.016	0.016	0.015	0.014
Cr	**0.315**	0.022	0.016	0.065	0.101	0.093	0.092
Pb	BDL	BDL	BDL	0.017	0.032	0.026	0.031
Hg	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se	0.072	BDL	0.096	0.052	0.083	0.060	0.016
Ag	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cu	0.103	0.020	0.119	0.105	0.326	0.061	0.048
Ni	0.132	5.289	5.568	5.389	5.486	5.674	5.600
Tl	0.013	BDL	0.017	BDL	BDL	BDL	BDL
V	**0.114**	BDL	BDL	BDL	BDL	BDL	BDL
Zn	0.337	10.349	10.564	10.895	10.845	11.255	10.997

*BDL= Below Detection Limit

The MWLP is helpful in determining the long term leaching behavior of wastes placed in acid environments. Many metals, such as aluminum, copper and lead may not be leached from the waste until the leaching fluid becomes very acidic. In the case of high alkaline wastes this may not happen until several volumes of acid water have come into contact with the waste product.

Comparisons of TCLP and MWLP leachates have shown that in many cases TCLP does not accurately predict the long term effect of wastes products on water quality when placed in acidic, metal-laden, aquatic environments. In addition, TCLP may overestimate the leaching potential of barium, particularly in steel slags. The benefits of MWLP are more apparent when dealing with high alkaline waste products, where a single leaching cannot effectively exhaust the alkalinity in the system. In these cases several leaching cycles are necessary in order to understand the leaching behavior of these wastes once all alkalinity has been exhausted and the leachate becomes acidic.

Table 9. Comparison of Indian Fly ash TCLP and MWLP leachate elemental composition. *This fly ash was leached with two different acid waters. The table shows the differences in leachate quality due to differences in raw water acidity and elemental composition. TCLP metal concentrations in bold exceed MWLP concentrations throughout the MWLP leaching period. Concentrations are in mg/L.*

Indian Fly ash		**Pit 1**	**Pit 1**	**Pit 1**	**Pit 1**		**Pit 2**	**Pit 2**	**Pit 2**	**Pit 2**
	TCLP analysis	MWLP Raw Water analysis	MWLP Cycle 1 analysis	MWLP Cycle 2 analysis	MWLP Cycle 3 analysis	TCLP analysis	MWLP Raw Water analysis	MWLP Cycle 1 analysis	MWLP Cycle 2 analysis	MWLP Cycle 3 analysis
pH	3.5	2.8	3.2	3.0	2.9	3.5	2.6	2.9	2.6	2.5
acidity	4458.8	675.8	756.1	680.0	833.1	4458.8	2128.0	2027.0	1995.0	2145.0
est. acidity	115.2	675.8	758.3	767.1	769.9	115.2	1812.1	2139.1	2115.1	2188.8
alkalinity	0.0	0.0	0.0	16.3	0.0	0.0	0.0	0.0	0.0	0.0
acid-alk	4458.8	675.8	756.1	663.7	833.1	4458.8	2128.0	2027.0	1995.0	2145.0
Mg	2.9	24.1	29.2	28.2	29.9	2.9	72.4	84.0	83.6	88.6
Ca	23.4	93.9	126.0	112.2	113.6	23.4	192.6	258.0	228.0	237.3
Fe	0.8	39.3	18.6	34.2	44.6	0.8	240.3	259.3	269.0	284.2
Al	17.0	86.0	120.3	110.3	104.5	17.0	181.6	242.6	222.9	226.2
Mn	0.4	3.0	3.6	3.3	4.2	0.4	10.6	12.8	12.0	13.1
Sb	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
As	**0.013**	BDL	BDL	BDL	BDL	0.013	BDL	0.076	0.035	0.065
Ba	**1.005**	0.043	0.133	0.111	0.107	**1.005**	0.028	0.194	0.073	0.078
Be	BDL	0.039	0.074	0.064	0.064	BDL	0.122	0.149	0.065	0.117
Cd	BDL	0.059	0.014	0.011	BDL	BDL	0.013	0.023	0.013	0.013
Cr	0.019	0.023	0.071	0.048	0.053	0.019	0.112	0.174	0.126	0.150
Pb	BDL	0.028	BDL	0.008	BDL	BDL	0.044	BDL	BDL	BDL
Hg	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se	**0.021**	BDL	0.015	0.012	0.012	0.021	0.037	0.049	0.019	0.028
Ag	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cu	0.129	0.047	0.409	0.013	0.121	0.129	0.169	0.478	0.187	0.224
Ni	0.112	0.973	1.986	1.879	1.692	0.112	3.257	3.746	2.931	3.285
Tl	BDL	BDL	0.007	0.005	BDL	BDL	BDL	0.013	0.007	BDL
V	0.137	0.492	0.030	0.035	0.059	0.137	0.013	0.285	0.155	0.177
Zn	0.349	5.730	6.136	5.771	5.284	0.349	11.800	10.707	7.414	9.242

*BDL= Below Detection Limit

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