

# THE MINE WATER LEACHING PROCEDURE

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## Abstract

Federal and State regulations encourage reduction of industrial waste streams to decrease the acreage consumed by landfills. In particular, applications that resolve environmental problems are recognized by State policy as “beneficial uses.” These large-scale projects may involve filling surface and underground coal mines with ash to address hydraulic problems, acid mine drainage, pit backfilling, and subsidence. In some States, those mine filling projects classified as beneficial are not subject to industrial waste disposal conditions such as liners, leachate collection, and monitoring. Coal Combustion Byproducts (CCBs) are attractive for such applications because they constitute a source of low cost alkalinity and favorable economics resulting from transport back to the mine in otherwise empty coal haulage trucks. The environmental risk of land filling CCBs is generally evaluated by the Toxic Characteristics Leaching Procedure (TCLP) or the Synthetic Precipitation Leaching Procedure (SPLP). However, there is doubt regarding the applicability of these tests to long-term CCBs leaching behavior in groundwater associated with coal mines. The Mine Water Leaching Procedure (MWLP) was developed to provide a site specific risk assessment tool. The MWLP procedure is presented in this chapter as a study case and comparisons with TCLP results were made.

## The Mine Water Leaching Procedure

MWLP was developed to determine the long-term leaching behavior of industrial wastes when placed in contact with the groundwater on a given site. The method sequentially leaches the CCB with a sample of the site’s groundwater until the alkalinity is exhausted and the pH of the leachate returns to that of the mine water sample.

The MWLP is applied identically for all waste products, differing only in the number of leaching cycles required for alkalinity exhaustion. This point is determined as the pH of the untreated mine water. A general outline of the procedure is included below:

- One hundred grams of fly ash were weighed out and transferred into 2-L plastic reaction bottles. To each ash sample was added one of two leachants: mine water or deionized water (control). Three replicates of each ash were prepared. The bottles were then sealed with Parafilm and the lids were secured. Reaction bottles were arranged evenly on a rotating platform, identical to that used in the TCLP test, and rotated end-over-end for 18 hours at 30 rpm.
- Following each 18 hour cycle the contents of each bottle were filtered through a 0.7 um glass, borosilicate filter using a stainless steel pressure filtration unit at or below 40 psi. A two liter container was placed under the base of the filtration apparatus to collect the filtrate. The contents of the fly ash + AMD reaction bottle were poured into the top of the pressure cylinder, the lid was secured and N<sub>2</sub> was introduced to pressurize the filtration unit. The pressure was slowly increased to 40 psi until all the liquid was removed from the unit.
- Following filtration the unit was disassembled and the filter cake (filter + solids) removed and saved for use in the subsequent cycle.
- Five hundred ml of each leachate was collected in two 250 ml bottles. One bottle was sent to an analytical laboratory for pH, acidity and alkalinity determinations using a Brinkman Autotitrator. The other bottle was acidified using 1 ml of 1N nitric acid and sent to the lab for elemental analysis (Sb, As, B, Ba, Cd, Cr, Pb, Hg, Ag, Cu, Ni, Tl, V, Zn, Mo, Fe, Mn, Al, and B) using a high resolution ICP-Mass Spectrometer.

- Solids collected during filtration were rinsed back into their corresponding reaction bottles with 2 “fresh” liters of leachant and placed back on the rotating platform for another 18 hour cycle. The leaching-agitation-filtration cycles continued until all alkalinity was removed from the system.

### Interpreting the Results

Leachate metal concentrations can be attributed to four possible sources: leachant (AMD), released metals from dissolution of the waste matrix; remobilized AMD metal precipitates; and remobilized ash metal precipitates (Figure 1). Since concentrations and volumes of leachant and leachate waters were known, it was possible to prepare a series of mass balances. So, by subtracting the elemental masses exported from the system (in the leachate) from the elemental masses imported to the system (in the AMD or leachant), it was possible to determine the net effect of ash addition on the concentration of toxic elements in the leachate. Table 1 shows the cumulative import, export, sequestration and release of Cr during a MWLP leaching series. This example indicates that between pH 4.2 and 3.8, the system stops sequestering Cr and begins releasing it.

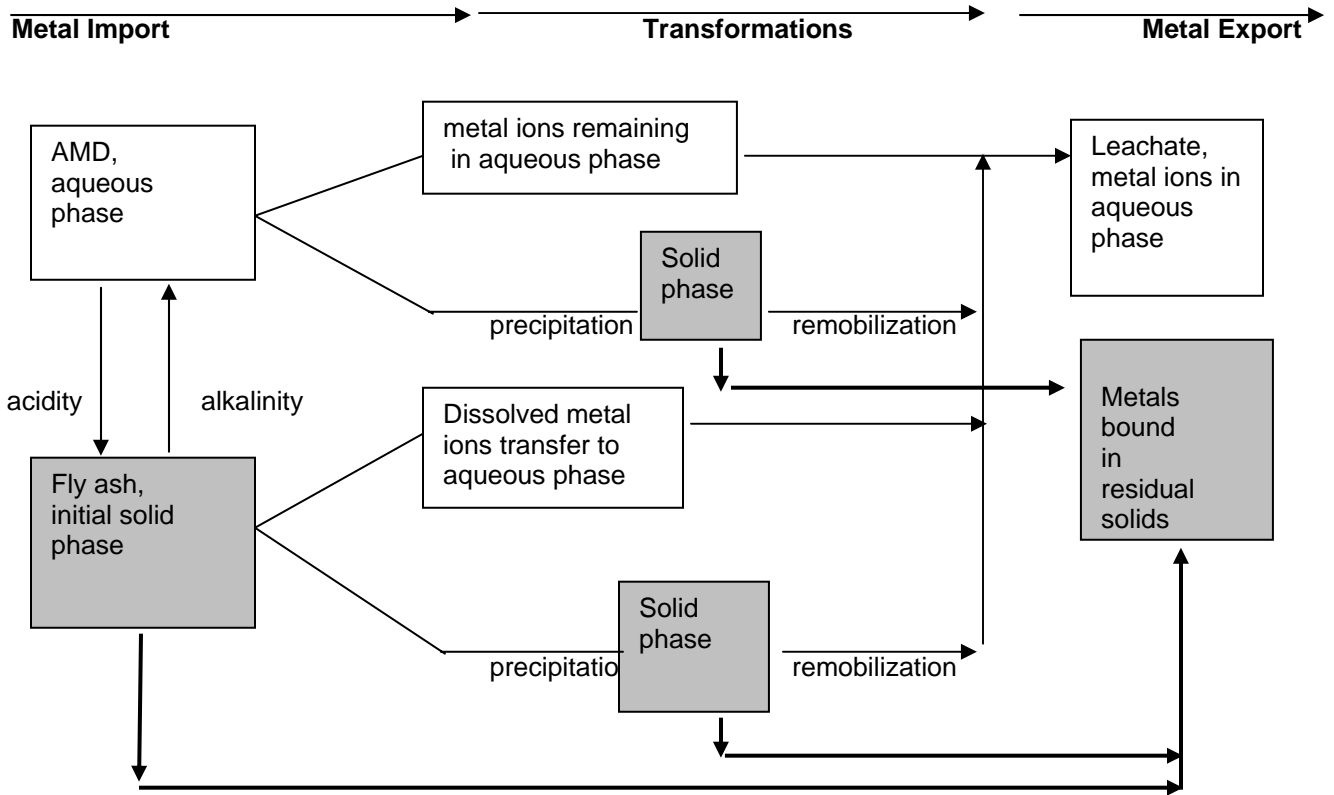


Figure 1. Diagram of the experimental system. Metals can be imported to the system from either the AMD (aqueous form) or fly ash (solid form). Once in the system, metals can either stay in the aqueous phase, precipitate into the solid phase or resolubilize into the aqueous phase.

Table 1. Example of Cr Import/ Export Table for Class F Fly Ash MWLP. All in, out and release values are cumulative. For example, the value of .180 mg for Cr In at Cycle 5 is the cumulative concentration of Cr in the import water (AMD) for cycles 1-5. The Cr Out is calculated similarly. This permits the calculation of the mg of cr released into the leachate water as a result of the fly ash addition to the AMD.

Cycle	Leachate pH	Cr In (mg)	Cr Out (mg)	Fly ash Release (mg)	% Released
1	4.17	0.044	0.032	-0.012	-28.0%
2	3.82	0.088	0.161	0.073	83.0%
3	3.54	0.132	0.362	0.230	174.3%
4	2.87	0.176	0.547	0.371	210.9%
5	2.92	0.220	0.732	0.512	232.5%
average					134.5%

### Discussion

The MWLP differs from TCLP in two ways. First, TCLP, uses standard synthetic extraction fluids, titrated to various pH ranges with acetic acid, MWLP uses water from the intended application site. It is expected to provide a more accurate simulation of field conditions than TCLP and accounts for chemical interactions between ions released from the CCB and those in the mine water. Second, TCLP uses a single 18 hr leach cycle while MWLP continues leaching until all alkalinity is exhausted. In the case of many CCBs, the TCLP stops while the pH is still strongly alkaline. While the intent of the CCB application may be to neutralize mine water acidity, the TCLP sheds no light on situations where re-acidification of the CCB mass is a possibility.

While MWLP is meant to simulate the likely chemical products resulting from exposure of a given CCB to a particular mine water, in its current configuration, it does not simulate reducing conditions. Additionally, MWLP simulates many years of weathering in a short period (roughly 32 pore water exchanges per leach cycle). It is important to remember that field concentrations of contaminants will be strongly influenced by the method of CCB placement, its volume, groundwater gradients, and spoil quality. Therefore, the concentrations yielded by the test are not expected to estimate concentrations under field conditions.

As pH and acidity change through the MWLP cycles, various elements appear in the leachate. In some instances, an element will appear for one or two cycles then drop below detection limits. This could indicate that an element is being sequestered or it could mean that its soluble fraction has been leached out of the fly ash. In either case, MWLP will highlight elements that may become mobile and the pH range in which it is likely to occur.

It is understood that the short 18 hour cycle time may not allow many intermediate mineral phases to come into equilibrium. Accounting for these phenomena and their significance over the long term are yet to be determined.

The MWLP is helpful in predicting the long term leaching behavior of wastes placed in acid environments. Many metals, such as Al, Cu, and Pb may not be leached from the waste until the leaching fluid becomes very acidic. In the case of highly alkaline wastes, this may not happen until dozens of pore water exchanges have occurred. The benefits of MWLP are most apparent when dealing with alkaline waste products, where a single leaching cycle will not exhaust the alkalinity in the system. In these cases, several leaching cycles are necessary in order to understand the leaching behavior of these wastes as its alkalinity is exhausted and the leachate becomes acidic. This is not meant to imply that all CCB minefills will become

acidic. Rather, it allows the user to evaluate leaching behavior through a range of pH conditions controlled by the pH of the leachant and the inherent alkalinity of the CCB.

## Conclusion

The Mine Water Leaching Procedure (MWLP) was developed to determine the long-term leaching behavior of industrial wastes in groundwater found on the potential application site. The method sequentially leaches the fly ash with a sample of the site's groundwater until the alkalinity is exhausted and the pH of the leaching solution is reestablished at its pre treatment level.

Import/export calculations showed the extent to which metals entering the leaching system via AMD were sequestered as solid phase precipitates. It appeared that precipitation and remobilization was a significant pathway for most metals.

A single MWLP cycle represents about 32 pore water exchanges. If one could estimate groundwater flux through the CCB mass, it would be possible to estimate the years required under field conditions to affect a single pore water replacement. This would allow placement of a temporal axis on the leachate data and further enhance the ability to predict risks associated with CCB placement in mine fills.

Elemental concentrations obtained via MWLP are unlikely to reflect actual field concentrations. They will also be influenced by the method of CCB placement, its hydraulic conductivity, the ability of the surrounding mine spoil to sequester toxic elements, adjacent ground water quality, and gradients. Nevertheless, MWLP is expected to provide an important component of the overall risk assessment picture.

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**Dr. Paul Ziemkiewicz** is the Director, West Virginia Water Research Institute, West Virginia University and the National Mine Land Reclamation Center. He has over eighty publications including publications on Coal Combustion By-Products related to coal mining issues. His most recent publications is on Prediction of Coal Ash Leaching Behavior in a Acid Mine Water: Comparison of Laboratory and Field Studies. His related associations include: Member, Board of Directors, National Environment and Education Training Center, Research Associate Professor of Plant and Soil Science, West Virginia University, Research Professor, Department of Biology, West Virginia University, Member, West Virginia Acid Mine Drainage Task Force, Member, Eastern Mine Drainage Federal Consortium, Technical Support Team Leader: Appalachian Clean Streams Initiative/Acid Drainage Technology Initiative, Member, National Research Council Study Team: Water Quality in the Pittsburgh Region, Member, West Virginia Special Reclamation Fund Advisory Council, and Member, Board of Directors, The Annapolis Center for Science-Based Public Policy. He holds a B.S. from Utah State University with a major in Biology and minor in Chemistry. He holds a M.S. from Utah State University in Range Ecology and a Ph.D. from the University of British Columbia in Forest Ecology.