



## Memorandum

To: Lisa Beckwith and Members of the VA CCP Regulation Technical Review Committee

From: W. Lee Daniels, Professor

Re: Fly ash leaching potentials and testing protocols

Date: August 8, 2008

Attach: 2006 OSM Leaching Trial Report by Daniels et al.

I am sorry that I will not be able to attend the next CCP TRC meeting on August 13; I will be on annual leave next week. Per your request in our first meeting, and due to recent interest in fly ash leachability issues in Chesapeake and other localities within Virginia, I am providing a brief synopsis here of my opinions on the leaching issue and appropriate analytical protocols. I want to apologize in advance for the length of this little document, but there is no simple way to approach these issues!

The use and management of CCP's has been one of my major research focus areas since the early 1990's, and I sat on the original DEQ CCP regulatory development committee in the early 1990's. More research details, publications and presentations of our work on this topic are available at: <http://www.cses.vt.edu/revegetation/>. It is **very important** to point out, however, that the majority of our studies have focused on fly ash materials that have been mixed with strongly acid-forming coal waste materials which is a very different geochemical environment from ash being placed into a monofill per the regulations under review by this committee. That being said, the basic geochemical controls on leaching that I discuss below are operable in both a mixed ash:mine waste environment and in ash monofills. We have also confirmed these basic relationships through leaching trials of pure ash, and similar results have been reported by other researchers in the literature.

First of all, I want to confine this discussion to the leachability of coal fly ash and not other CCP's such as FGD. We have performed detailed analyses on over 50 regional coal fly ash samples to date and data on recent chemical analyses performed on 28 (primarily fly ash) samples from utilities burning Virginia coal are provided in the attached research report. In Table 1 of that report you will note that the electrical conductivity (EC) of saturated water extracts from fly ash generally ranges from 2 to 12 ds/m (or mmhos/cm). This parameter is also commonly referred to as "soluble salts" which are dominated by sulfates in fly ash:water solutions. To put this into perspective, native soils in Virginia seldom exceed 0.2 mmhos/cm and values exceeding 4 mmhos/cm are detrimental to most plants as demonstrated in the greenhouse study portion of the attached research report. Therefore, the vast majority of fly ash materials that we manage in any structural fill application or land application scenario can evolve a significant load of soluble salts to leaching waters over time. The EC or concentration of those salts decreases over time, and is always highest as the first pore volumes of water exit the material. For this reason, when fly ash is used in large volumes such as in

structural fills, it is important to (A) isolate it above the seasonal (winter) high water table and (B) limit water infiltration down through it. The current regulations contain language that directly addresses point A and indirectly addresses point B.

As stated above, the vast majority of soluble salts and constituents that will leach from any fly ash will be soluble sulfates which generally do not pose a direct health risk. Secondly, boron (B) is seen in almost all fly ash leachates (as the borate anion) at significant ( $> 1$  mg/L) levels, but to date has not been considered to be a significant water quality or health risk. Of greater public and regulatory concern is the potential for heavy metals like Cu and Pb, and/or oxyanions of As, Mo and Se to leach in association with these other salts as the emplaced ash materials weather over time. In general, as long as the bulk pH of the geochemical environment is held above 5.5, we expect to see very limited (if any) mobility of Cu, Ni, Pb, Zn and other heavy metals into leachates. Similarly, as long as the pH of the ash matrix area is below 8.5, we expect limited mobility of oxyanions of As, Mo and Se. However, the negative effects of bulk pH being outside of this range (5.5 to 8.5) are clearly demonstrated in the attached report and in similar journal articles and reports available from our website. Simply put, we see heavy metals leaching from ash exposed to strongly acidic environments ( $< \text{pH } 4.5$ ) and oxyanions like arsenate, molybdate and selenate leaching from ash exposed to strongly alkaline ( $\text{pH} > 9.0$ ) environments when they are present at elevated levels and in soluble forms. That being said, *we see clearly beneficial net water quality effects of the appropriate use and mixture of alkaline fly ashes into acid-forming coal waste materials* and we continue to support that practice. Similarly, we see beneficial effects of the application of relatively low rates ( $\leq 50$  tons/acre or 5% by volume) of fly ash to soils as a topical soil amendment as long as bulk soluble salts immediately after land application are kept to levels that don't suppress plant growth.

In contrast to the coal mining fill environments discussed above, the bulk pH and geochemical environment of fly ash monofill leachates will be controlled directly by the properties of the ash itself (plus any additives like cementitious binders) and **not** by the properties of surrounding wastes or soils. As rain water slowly percolates down through the ash fill, it will be strongly buffered by the soluble salt phases and reactive surfaces of the ash, and for some extended period of time, the leachate will be relatively high in EC, sulfates and other elements as controlled by the basic pH-solubility relationships discussed above.

In addition to bulk solution pH, the total mass (concentration) and form (speciation) of elements of concern in fly ash also directly affects their mobility or potential "leachability". As can be seen from the data presented in Table 2 and Figure 1 of the attached report, any element of concern (e.g. As) can be found in widely varying levels and relative forms, and fly ash tends to vary strongly from source to source in bulk concentration and speciation of many elements. Of particular importance are forms which are more readily soluble or "bioavailable" which are represented in Figure 1 as the "Exchangeable" and "Carbonate" bound forms.

Now, I will finally address the issue of testing ashes for their relative "leachability". As can be inferred from the above discussion along with a brief perusal of our reports and journal articles, I strongly favor the use of leaching column analyses to predict field behavior. That being said, leaching columns are expensive to conduct, take many months to perform, and generate worse-case data sets relative to actual field observations. Therefore, leaching columns are not a practical

solution for the routine screening of ash for proposed monofill projects. The most common alternatives are what are known as “batch extraction” techniques where the ash is equilibrated with a liquid extractant (e.g. an organic acid like acetate) and then elements of concern like As and Pb are analyzed in those extracts. The USEPA Toxicity Characteristic Leachate Procedure (TCLP) is the most commonly employed of these. For the TCLP extract, the concentrations of metals and other inorganic/organic toxicants are then compared to a reference value which is scaled (e.g. 100 to 1000x) against the applicable drinking water MCL. This supposedly allows for anticipated effects of contaminant dilution and attenuation down the migration pathway. In 15 years of testing we have never seen a fly ash sample “flunk the TCLP test”, but we have seen a number of those same ashes elute significant amounts of elements of concern when subjected to strongly acidic or alkaline leaching environments. Of all the various extracts and techniques that we have screened to date, we believe that the modified sequential extraction procedure (see Fig. 1 of attached report), and particularly the sum of the exchangeable+carbonate fractions is probably the most accurate technique for predicting relative risk of a given element solubilizing and leaching over time. However, in order for this to be used as a screening tool for ash monofill projects, we would have to come up with appropriate multipliers as used with the TCLP test to account for anticipated attenuation and dilution.

At our last meeting, Jeff Stant mentioned that a number of federal agencies have been considering the Kosson et al. (2002) procedure for screening ash leachability. We have tested this procedure in our labs and do not think that it is applicable here for a number of reasons. First of all, the procedure involves many serial extractions with varying pH and solid:extractant ratios and is very expensive. Perhaps more importantly, this test was designed to estimate what will happen to a given ash subjected to a wide range of pH environments encountered in mining or other land disturbance environments. In an ash monofill, as discussed earlier, the ash itself is going to directly control leachate chemistry, so the use of the wide range of extractant conditions as utilized in this test just doesn't make sense. On top of that, critical extract thresholds for various elements in the procedure have yet to be developed.

So, the bottom line here is that we simply do not have scientific agreement on what test is the best predictor of fly ash leachability. However, what we clearly do know is that if rainfall is allowed to percolate down through an ash monofill, it will become enriched in certain salts like sulfate and borate. Under certain conditions (e.g. very high pH + high concentration + high bioavailability), elements of concern like As can also dissolve into these leachates. Once these dissolved compounds leach below the bottom of the ash layer, they will be subjected to a number of potential attenuation and/or sorption pathways, but those are beyond the scope of this memo.

Therefore, I am of the strong opinion that we really shouldn't focus in the short-term about what tests beyond the TCLP we should be using to discriminate among ashes, **we should focus on limiting water migration into and through the ash.** Thus, I believe that the ash should either be capped with a relatively impermeable barrier or the ash should be compacted and/or treated *in situ* to directly limit internal permeability. The early proposed language of the original version of the CCP regulation under review here contained a recommended minimum permeability specification of  $10^{-5}$  cm/S, but that provision never made it into the final regulations. I would suggest that any revisions

to this regulation should include a similar or more rigorous permeability standard. To that end, most fly ash materials that we have worked with can be readily compacted to approach or exceed this permeability standard. The appropriate addition of a cementitious binder can also accomplish this, and certain fly ashes are pozzolanic or “self-cementing” in themselves. Finally, the mandatory two foot standoff between the bottom of the ash monofill and the seasonal (winter) high water table should be rigorously reinforced with language to specify acceptable field verification methods (e.g. wells/piezometers and soil morphology) to certify that essential separation.

I appreciate your patience in wading through this little memo and I will be glad to follow-up on any questions raised at our next committee meeting. I can also be contacted as shown in the page 1 letterhead on or after August 18.

References: Kosson, D.S., H.A. van der Sloot, F. Sanchez, and A.C. Garrabrants. 2002. An integrated framework for evaluating leaching in waste management and utilization of secondary materials. *Env. Engineering. Sci.* 19:3, 159-204.