Message

**From**: Tuori, Thomas [ttuori@hselaw.com]
**Sent**: 8/16/2017 8:43:43 PM
**To**: Daly, Eric [Daly.Eric@epa.gov]
**CC**: Ludmer, Margo [ludmer.margo@epa.gov]
**Subject**: Radioactive Slag -- Fingerprinting Analyses [HSELAW-WORKSITE.FID715352]
**Attachments**: DEC Fingerprintng Analyses 9524 and 9540 NF Blvd and Cemetery.PDF; DEC Metals and Minerals Analyses 2008 Emlab Data.PDF; Union Carbide Slag Composition Data 1960s - Excerpt.PDF; 1981 Oak Ridge Report - Love Canal - Schools - Oldbury Furnace.PDF

Hi Eric,

I am responding to your email dated August 9th and your request for input regarding fingerprinting analyses.

Please see below for some high-level thoughts on this topic. The information summarized below is based on our research over the last several years. This information will provide a useful roadmap as we move forward with our fingerprinting efforts.

If you and Margo are amenable, I would like to schedule a follow-up call to discuss the information summarized below and related matters.

- **Metals.** Metals analyses should include uranium, thorium, tantalum, titanium, vanadium, zirconium, and rare earth metals. I believe these are captured by EPA Method 6020A (ICP/MS, inductively coupled plasma mass spectrometry). Since the metals are likely bound up in silicate-based slag structures (such as calcium-silicate), it does not appear that digestion by Method 3050b will be appropriate or effective. Our understanding is that digestion via EPA Method 3052, perhaps with microwave assistance, would be more appropriate and effective. A variety of digestion methods may need to be tried to determine the most effective approach.

  Here are a few other thoughts to consider:
  1. My understanding is that the EPA's prior sampling (by the NPL evaluation team) at the Niagara Falls Blvd. properties and at the Holy Trinity Cemetery did not include any metals analyses. EPA's prior sampling at the Talarico/Grace properties included metals analyses, but only for TAL metals.
  2. Sampling by NYSDEC in 2008 at the Niagara Falls Blvd. properties and at the Holy Trinity Cemetery identified zirconium at levels in the single-digit percentages, which is far above the typical background levels. See the two attached "DEC . . . " pdfs. I sent these to Margo in July. Our research indicates that certain companies in the Niagara Falls area, including Union Carbide (in Niagara Falls) and Stauffer Chemical (in Lewiston, just south of the Holy Trinity Cemetery), were producing zirconium alloys and/or other zirconium compounds in the 1950s and/or 1960s.
  3. The detection of niobium and/or tantalum would be very helpful for fingerprinting purposes. Our research indicates that Union Carbide and Stauffer Chemical were producing niobium and tantalum alloys and/or other niobium and tantalum compounds in the 1950s and/or 1960s.
  4. Generally, if a certain non-ubiquitous metal is found within a slag sample, then that would be strong correlation between the slag and a specific metal product (or waste) that a specific company may have been generating. For example, trace amounts of zirconium, niobium, tantalum, vanadium and/or rare earth metals in a radioactive slag sample would strongly suggest that the original source material came from a deposit/ore that was mined for -- or at least contained appreciable amounts of -- that metal. The company known for generating a product or a waste that contained the metal would clearly be implicated as the generator of that particular slag.

- **Phosphorus and other elemental analyses.** Proper analyses should be conducted to detect phosphorus down to 0.1%+ levels. If elevated levels of phosphorus are detected, then that would strongly suggest that Oldbury (successor is Occidental Chemical) is the source of the slag. (Oldbury produced phosphorus at a plant on Buffalo

Avenue in Niagara Falls and slag waste was generated in that operation. Our research indicates that phosphorus slag typically contains 0.5% to 3.0% $P_2O_5$.) I have seen references to use of SEM-EDS (scanning electron microscope with energy dispersive spectrometry) analyses to detect phosphorus and other elements, but don't know if that is the best approach.

Also, if the predominant elements in the slag are calcium, silicon, and oxygen, then that would also strongly suggest that Oldbury is the source -- especially if phosphorus was also found and if mineralogical analyses indicates that the slag structure is pseudo-wollastonite/cyclo-wollastonite. See, for example, the attached "1981 Oak Ridge Report . . . " pdf, which concludes that slag from an Oldbury phosphorus furnace was pseudo-wollastonite/cyclo-wollastonite (based on 'petrographic' analyses).

My understanding is that the SEM-EDS analyses would also identify individual metal elements, such as those discussed in the "Metals" bullet item above. It appear that the NYSDEC's sampling in 2008 used SEM analyses.

- **PLM to determine glass vs. crystalline structure.** The PLM (polarized light microscopy) step is used to determine the glass and crystalline content of the sampled material. Our understanding is that you would follow up with XRD (x-ray powder diffraction) analyses to determine the mineralogical content of the crystalline component.

- **XRD to determine mineralogical content.** As noted above, if pseudo-wollastonite/cyclo-wollastonite is identified by XRD analysis, then that would strongly suggest that Oldbury is the source of the slag. Other mineralogical results may indicate that the slag resulted from the production of niobium, tantalum, zirconium and/or other metals.

- **Ratios of certain oxides.** As you may be aware, there is historic Union Carbide data which lists the percentage of certain oxides in slag generated during its production of niobium. See the attached "Union Carbide . . . " pdf. In addition, pseudo-wollastonite/cyclo-wollastonite is comprised predominately of $CaSiO_3$. So, having data on the oxide composition of the slag would be very helpful for fingerprinting purposes. I do not know the best analytical approach for determining oxide composition.

- **Radiological fingerprinting.** We have seen sample results which indicate that Oldbury slag did not include appreciable amounts of thorium (and that radium and uranium were roughly in equilibrium).

With respect to any sampling by EPA at our clients' properties, we would appreciate the opportunity to review and comment on your proposed sampling plans, analytical methods, and sample digestion methods. Also, we intend to have a technical consultant observe your sampling and, if sufficient sample material is available, we would like to collect split samples.

Please let me know when you are available for a call to discuss these matters.

In the interim, please let me know if you have any questions.

Thank you,
Tom

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