DOI: 10.1017/S1431927605504069
Microsc Microanal 11(Suppl 2), 2005

Application of Scanning Electron Microscopy to Characterization of Radioactive Solid Wastes from Underground Storage Tanks

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Performance assessments will be completed to evaluate the long-term health risks associated with closure of 177 single- and double-shell carbon steel-shell underground storage tanks containing residual radioactive and toxic wastes at the U.S. Department of Energy's (DOE) Hanford Site in southeastern Washington. The primary contaminants of concern for the Hanford Site are typically ^{99}Tc, ^{238}U, ^{29}I, and Cr because of their mobility in the environment and long half-lives. PNNL is currently developing source term models that describe the release of contaminants as infiltrating water contacts the residual solids. To simulate the geochemical interactions between the leachant phase and contaminant-containing solids, these models must be based on detailed characterization of the residual waste. Because these sludges are highly radioactive, dispersible powders and are chemically-complex assemblages of crystalline and amorphous solids that contain contaminants as discrete phases and/or sequestered within oxide phases, their detailed characterization offers an extraordinary challenge to electron microscopists, geochemists, and laboratory-safety engineers.

Scanning electron microscopy/energy dispersive spectrometry (SEM/EDS) and X-ray diffraction (XRD) are the two principal methods being used to characterize solid phases and their contaminant associations in these sludges. SEM/EDS and XRD have been completed on as-received (unleached) samples as well as residual solids obtained from water leach studies and selective extractions designed to isolate the principal phases that control the release of each contaminant of interest. Because many contaminants of concern are heavy elements, SEM analysis using the backscattered electron (BSE) signal has proved invaluable in distinguishing phases containing elements, such as U and Hg, within the complex assemblage of particles that make up each sludge. Figure 1 shows micrographs for sludge samples from Hanford tanks C-203 and C-204 [1]. Because these images were obtained using the BSE signal, the hexagonal needlelike crystals containing Na-U-O in Figure 1A are clearly distinguishable from the Na-Al-P-O and Fe-Cr-Ni oxide phases that make up the sludge matrix. The morphological features and EDS data for these needlelike crystals were consistent with the XRD identification of cejkaite [$Na_4(UO_2)(CO_3)_3$] in this sludge. Figure 1B shows the same sludge material after a 2-week water leach. This BSE micrograph also allows quick identification of the U-containing solids relative to the rest of the sample matrix. It also shows that the cejkaite needles dissolved during the water leach, but a second, less soluble, amorphous-looking U-Na-O phase [possibly $Na_2U_2O_7$ or clarkeite $Na[(UO_2)O(OH)](H_2O)_{0\text{-}1}$] was present in the residual sludge and will impact the long-term release of U from this residual waste.

SEM/EDS and XRD also provide different, but complimentary characterization data, which help determine the morphologies, particle sizes, surface textures, and compositions of phases in sludge. Their impact is greatly magnified when each technique is used in an iterative fashion to cross interpret the results from the other analysis method and then identify additional, more refined SEM/EDS and XRD analyses to be done. This strategy was necessary, for example, to refine analyses of the SEM/EDS and XRD results to identify the complex assemblage of solids for as-received sludge from tank C-106 [2]. These phases included gibbsite [$Al(OH)_3$], boehmite [$AlO(OH)$], dawsonite [$NaAlCO_3(OH)_2$], Fe-Cr and Fe-Mn oxides such as hematite (Fe_2O_3), possibly two different Mn-O-C±H phases based on morphology such as rhodochrosite ($MnCO_3$) and lindbergite ($MnC_2O_4{\cdot}2H_2O$), whewellite ($CaC_2O_4{\cdot}H_2O$), possibly 1one or two phases with Ag-Hg±Fe±Pb±Cu, an REE-rich oxide, and unknown Mn-Al-Fe-Na-P-Si-Ca-O±C±H phase. The SEM/EDS analyses were able to confirm the phases identified by XRD and refine the search options when trying to resolve the XRD patterns.

Application of SEM/EDS, especially in BSE mode, in combination with XRD has proved to be invaluable in providing the necessary solid-phase characterization data needed to develop source term models for simulating contaminant release from residual radioactive and toxic wastes that may remain in decommissioned underground storage tanks.

References

[1] W. J. Deutsch et al., Hanford Tanks 241-C-203 and 241-C-204: Residual Waste Contaminant Release Model and Supporting Data. PNNL-14903, PNNL, Richland, WA, 2004.
[2] W. J. Deutsch et al., Hanford Tank 241-C-106: Residual Waste Contaminant Release Model and Supporting Data. Report in final review, PNNL, Richland, WA, 2005.
[4] The authors wish to acknowledge M. Connelly and F. J. Anderson at CH2M HILL Hanford Group, Inc. (Richland, WA) for providing project funding and technical guidance. Pacific Northwest National Laboratory is operated for the DOE by Battelle Memorial Institute under Contract DE-AC06-76RL01830.

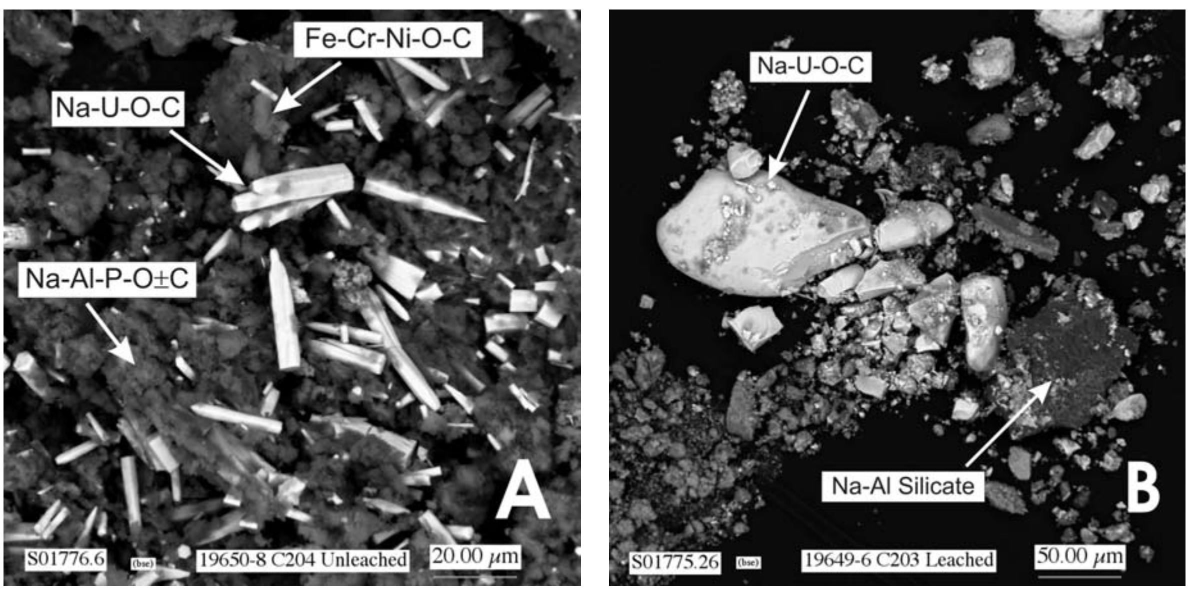

Fig. 1. SEM BSE micrographs showing particles present in unleached (A) and water-leached (B) sludges from tanks C-204 and C-203 [1]. [All "bright" particles contain U.]

https://doi.org/10.1017/S1431927605504069 Published online by Cambridge University Press