Project 60075

Particle Generation by Laser Ablation in Support of Chemical Analysis of High Level Mixed Waste from Plutonium Production Operations

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Problem

Thousands of tons of nitrate-based, high level mixed wastes from cold war plutonium production operations require real-time, on site characterization, both before and after incorporation into stable waste glasses. Laser ablation-inductively coupled plasma mass spectroscopy (LA/ICP-MS) systems have been developed for elemental and isotopic analysis with minimal sample handling at several DOE laboratories, including Hanford, Los Alamos, and INEEL. Research into the fundamental physical processes of particle formation during laser ablation is required to maximize the utility of these systems. Crystalline and polycrystalline nitrates interact weakly with most laser radiation and present special analytic challenges. Interactions with waste glasses must be understood to insure a homogeneous, stable waste product.

Research Objective

To provide fundamental mechanistic studies of laser-produced particulate formation in support of the analysis of radioactive and/or toxic materials by Laser Assisted–Inductively Coupled Plasma Mass Spectroscopy (LA/ICP-MS).

Research Progress and Implications

As of March 1, 2000 (six months remain in a three year project), we have characterized particle generation mechanisms laser ablation and their consequences in subsequent analysis by ICP-MS for model nitrates and waste glasses.

At typical laser power densities, analysis of both nitrate and waste glass materials show less scatter when UV laser wavelengths are employed. Work at PNL focused on waste glasses, because its more consistent response to laser irradiation facilitates comparisons among various treatments.

UV irradiation of waste glasses produces principally ultrafine aggregate particles which are readily digested in the plasma torch. However, EDX measurements on collected particles show significant deviations from the initial waste glass composition. These ultrafine particles are condensed from vaporized glass, where some glass components may preferentially vaporize and condense. High power density IR radiation produces many large fractured particles and large melted particles (> 2 µm in diameter) . These particles are not readily digested in the ICP-MS plasma torch, and may account for the relatively high scatter in LA/ICP-MS analysis when IR wavelengths are employed. However, EDX measurements of sample composition show that the composition of the fractured and large melted particles are quite similar to the waste glass composition.

The change in particle production mechanism as one moves from IR to UV wavelengths can be understood in terms of a thermal model of laser interaction. Both waste glass and the nitrates absorb much more strongly in the UV than in the IR. UV radiation heats a thinner layer of material to higher temperatures, allowing for efficient vaporization, followed by condensation into ultrafine particles. This process produces small particles that are readily digested in the ICP plasma, but also changes the particle composition.

Concurrent WSU focussed on the more intractable nitrates, using Cs- and Sr-doped single-crystal sodium nitrate as a model material. This effort examined the possibility of producing small fracture particles that can be analyzed reliably by ICP-MS. Three laser conditions were compared: high power density UV radiation (355 nm, particles principally condensed from vapor), high power density IR radiation (1064 nm, both melted and fractured particles), and low power density IR radiation (1064 nm, *principally fractured particles*).

High power density UV irradiation alters $NaNO_3$, quickly increasing UV absorption (incubation) and depleting volatile components (e.g., Cs). Although incubation and depletion are not desirable, the small particles produced by UV laser irradiation are more completely digested in the ICP-MS torch than the larger particles produced by IR. High power density IR irradiation depletes Cs relative to Sr; large fractured and large melted particles are produced. As expected, neither incubation nor Cs-depletion are observed under low power density IR irradiation. Nevertheless, the particle size distribution was similar to that obtained at high IR power densities. However, the fracture particle size distribution evolves towards smaller particles as irradiation progresses.

Planned Activities

In the remaining six months of this project, we will continue to develop models for particle fracture and condensation to improve our fundamental understanding of particle generation and to provide guidance for optimization.

Studies will also be made of the ablation of conglomerate-type samples comparable to the saltcake found in the Hanford waste tanks. These samples are composed of particulates that range from less than one micron to hundreds of microns. Salt-cakes typically possess structure on a wide range of size scales, which should result in the generation of significant quantities of sub-micron particles by fracture. In addition, we will investigate large particle exclusion strategies (filters, cyclones, etc.)

Information Access

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