

PHYSICO-CHEMICAL DYNAMICS OF NANOPARTICLE FORMATION DURING LASER DECONTAMINATION AND CHARACTERIZATION

Research Objectives

Improvement of understanding on nanoparticle production during simultaneous laser-based decontamination and characterization is imperative to the acceleration of decommission and deactivation (D&D) missions of US Department of Energy (DOE). Many researchers, mostly in material research, have explored issues related to aerosol particle formation by laser ablation, but there are little data relevant to D&D. Nanoparticles are harmful to D&D workers and the environment. The formation, properties, growth and transport mechanisms of radionuclides and toxic metals – laden nanoparticles are little known. The focus of this research is to investigate the effects of the laser parameters and the chemistry of target samples (contaminated and uncontaminated) on the dynamics and properties of produced particles. Data will facilitate better design of pollution control strategies. There are three goals associated with achieving the required understanding of nanoparticle dynamics.

- (1) To develop baseline property data of laser-produced nanoparticles from samples of different bulk chemical composition and surface morphology. The data would include properties of particles such as the size, shape, distribution, and chemical composition.
- (2) To develop advanced particle instrumentation (for sizing and chemistry measurement) so that reliable data can be obtained in higher resolution and shorter interval to delineate the dynamics, and
- (3) To employ an advanced computer simulation model to analyze and/or predict the dynamics of particles produced.

Research Progress and Implications

This section summarizes work performed after 9 months of a 3-year project. The bench-scale aerosol chamber that can be operated in a number of conditions, including low vacuum, was fabricated and rigorously tested for low particle background using a differential mobility analyzer and a light scattering technique. The performance of a scanning mobility particle spectrometer (that can provide measurement of particle size distribution and total number concentration of particles) and an ultrafine condensation particle counter (that yields total number concentration only) have been evaluated in terms of providing measurement for total number concentration of particles. A maximum difference of 20% coefficient of variation was found between the two systems when total number concentration reached about 10 millions per cm^3 . At concentration lower than 10,000, two systems yielded virtually identical data suggesting coincidence error plays a role leading to the large variation in the high-concentration measurement.

The fourth harmonic of a Nd:YAG laser was used to emit 266-nm wavelength energy used in the laser evaporation during the past 9 months. Nanoparticles and larger ones were formed during the laser evaporation process on concrete sample discs. Uncontaminated, no metals or radionuclides doped, concrete samples were made from the Portland cement. The sample was made initially without aggregate, cured under moist conditions for a minimum of 30 days, and then air dried for a minimum of 1 week before use. The construction-grade concrete is often composed of a cement binder and aggregate, which is usually in the form of small rocks of mixed composition (such as quartz and limestone).

We found that, in general, the higher total laser energy (i.e., in a single shot or totaled in a number of weaker shots in a given time) used the greater the total number concentrations of particles yielded. The peak size (i.e., diameter) of the generated particles remained in between 100 and 200 nm with smallest diameter we measured around 2 nm and largest in micrometer size range depending upon experimental conditions. The variation of the peak size for a given energy level was larger at larger laser energy. Two sources of particle formation were identified that are (1) direct formation by the laser (i.e., the primary particles) and (2) formation through coagulation/coalescence from the seedling nuclei during the first few seconds or faster (i.e., the secondary

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particles). The dispersion of the size distribution was relatively constant at a value of approximately three. Since the chemistry of sample remained identical, we expected this to hold until we use samples of different chemical composition in the second and third years. Higher laser energy did provide much more nanoparticles, those smaller than 50 nm in diameter, than that produced by lower energy. High number of particles also resulted in large measurement uncertainties by the instrument systems described above. The number concentrations produced under various laser energy conditions were found to be non-linear. The relationship between the number of particles produced and energy deposition frequency varying from 1 shot in every 150 seconds to 10 Hz (1500 shots in 150 seconds) of the 4th harmonic energy were also found to be non-linear and have a threshold at the lower end.

Co-PI, Dr. Da-Ren Chen of Washington University (WashU) in St. Louis, has completed the design and sent the drawing to a workshop for fabrication in May 2002. This novel design is brand new and not available on the commercial market. The design enables great flexibility in operation and measurement for a wide range of nanoparticle sizes. The fabrication is expected to be completed in July/August timeframe. The unit will then be tested at Dr. Chen's laboratory at WashU, and will be transferred to the PI at ORNL for use in the winter of 2003.

Planned Activities

For this fiscal year, we will finish the experiments using a second harmonic (i.e., 532 nm) and part of the work by the fundamental wavelength (i.e., 1064 nm). The data will be analyzed and the results will be compared with those of the 266-nm wavelength. The preliminary results will be presented in the upcoming annual meeting of the American Association for Aerosol Research (AAAR) in October. Consideration will be given also to publish the results in a peer-reviewed journal after AAAR.

For the next fiscal year (FY2003), an electrostatic precipitator currently being built in June 2002 will be employed to collect the nanoparticles for SEM/TEM analysis for morphology analysis. Time-resolved laser-induced breakdown spectroscopy will be used to analyze, on-line, the chemical composition of particles generated. Combining the particle size information, we would be able to produce the size distribution of various metals embedded in the particles. Chromium-doped target samples will also be used in 2003. The new DMA being developed at WashU will be employed to probe the particle dynamics on a shorter time scale (sub milliseconds). This will require reconfiguration of a window on the current aerosol chamber to house an equilibrium conduit for hosting the new DMA. Control electronics and software for running the DMA will also be developed and tested. Individual modules of the simulation model will be developed and/or collected from various sources and debugged. Initial runs will be made and the results will be compared to the data generated in 2002 and 2003.

For the final fiscal year (FY2004), similar experiments to those conducted in FY2002 and 2003 will be performed using radionuclide-doped target samples. After all the computer program modules for simulating particle dynamics are completed, the overall program will be evaluated. Prognosis using the simulation model will be undertaken. A particle control strategies and engineering design will be developed. A final report will be prepared.

Information Access

Yining Lin, a postdoctoral student working with the PI and the PI has submitted a paper to be presented in the Annual Meeting of the American Association for Aerosol Research in October. A novel aerosol spectrometer developed by the PI in an earlier project has been awarded a US patent # 6,359,687 in April 2002. This technology will be used in the second year to measure the composition of particles generated.