DOE/OBER EMSP Project #82807

Physico-Chemical Dynamics of Nanoparticle Formation during Laser Decontamination

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Research Objective: Laser-ablation based decontamination is a new and effective approach for simultaneous removal and characterization of contaminants from surfaces (e.g., building interior and exterior walls, ground floors, etc.). The scientific objectives of this research are to: (1) characterize particulate matter generated during the laser-ablation based decontamination, (2) develop a technique for simultaneous cleaning and spectroscopic verification, and (3) develop an empirical model for predicting particle generation for the size range from 10 nm to tens of micrometers. This research project provides fundamental data obtained through a systematic study on the particle generation mechanism, and also provides a working model for prediction of particle generation such that an effective operational strategy can be devised to facilitate worker protection.

Research Progress and Implications: This report summarizes work performed from FY02-05. A technique has been developed for simultaneous surface cleaning using laser plasma and contaminant verification using the plasma emissions. The effects of laser treatment (ablation) on surface decontamination were systematically examined. The decontamination technique does not produce highly contaminated secondary liquid waste that could be produced when an alternative technique such as a wet scrubbing method is employed, because this new technique is based on a dry process. This new decontamination technique also does not produce large quantity of contaminated rubles generated from mechanically knocking down contaminated building/wall and removal. The new technique will save both time and cost by preventing removal of an unnecessarily large quantity of materials during decommission and decontamination of DOE facilities by focusing on small-area treatment instead of entire building. The new technique will save a significant amount of analytical cost because it can characterize the effectiveness of surface decontamination in real time; thus, it does not create a latent and undesired waiting period for decision making and material transport off-site.

Over the past four years, a large volume of experimental data has been collected at the Laboratories of Aerosol Research (ARL) at ORNL for cement, stainless steel, contaminant-added cement, and alumina. The first three materials are commonly found in the DOE complex, while the last material was included for fundamental processes research. Use of a single-component material such as alumina enables us to minimize the complication of predicting multi-component chemistry in the formation of nanoparticles. Analyses indicate that the particles produced during decontamination by laser-ablation process are ultrafine ($D_p < 100$ nm) and fine particles ($D_p < 1{,}000$ nm) and the generation of a bi-modal distribution of particle size depends on both the material and the wavelength of laser used. The number of mode of the distribution does not depend on the laser energy. Rarely, particles with an aerodynamic diameter greater than 1 micrometer were found. Stainless steel, for example, does not produce super-micron size particles with respective to laser wavelength and fluence. Instrumentation data from a commercial scanning mobility particle sizer, a research-grade nano-aerosol sizer, and TEM are consistent and all indicate that no supermicron particles were generated by stainless steel.

The SMPS size distribution data indicate that the particles are uni-modal, and the mode diameters ranged from 20 to 200 nm depending on the ablation conditions regardless of whether or not plasma was formed. The production of plasma during surface treatment during laser ablation creates substantially different effects from that when no plasma id formed. The effects observed are multifaceted and include thermal, photochemical and photomechanical changes that typically result in a broadened size distribution. We have investigated particle formation over a wide range of laser fluence. At a lower fluence, no plasma was formed but ultrafine particles could still be formed. The mode diameters were generally around 20-30 nm, irrespective of laser wavelength and materials. Both ultrafine and fine particles were formed when plasma was generated by a high fluence, and the mode diameters were in the 70-90 nm irrespective of laser wavelength and materials.

The number concentrations of particles produced varied significantly depending on how and what type of laser energy was used. The concentration varied over nine orders of magnitude, from 10^3 to 10^{12} cm^{-3}. Based on the size of particles alone, a high-efficiency particulate air (HEPA) filter could remove a large percentage of the laser generated particles (LGP). However, the wide range of particle number concentrations identified in our study indicates that a control strategy will have to be designed to manage a decontamination process such that a HEPA filtration can operate optimally. The nanoparticles whose electrical mobility diameter smaller than or equal to 10 nm may not be effectively removed by filtration techniques; no data are available regarding the efficiency of existing filters. Thus, these extremely small particles will have to be controlled by other techniques that are beyond of this research project.

We also found that the capacity for generating particles for all the test materials (i.e., cement, stainless steel, and alumina) was highest in the UV wavelength range as compared to visible and IR, which is not a surprise considering material-laser coupling efficiency of the UV wavelength. The results support the fact that the UV wavelength should be the choice for surface decontamination. A database for particle generating capacity by laser treatment was created, and a empirical working model was developed that enables the use of the database in predicting the number of particles that could be generated from the surface treatment. The model can also provide the rate of particle generation, critical data for computer simulation. The information that is available from the model and database will prove useful in the application of laser ablation for surface decontamination. The test procedure may also serve as a protocol for future application of laser treatment of material surfaces in future research.

Planned Activities: This 3-year project was nearly completed by FY2004, but we were committed by the EMSP program to finish analyzing all the data and complete the project by the end of the fourth year (FY2005). Remaining activities for this project beyond FY2005 are a pending patent and manuscripts in review, which we expect them to be completed in FY2006 at no cost to the program office.

Public Information Access: We had been productive during the past four years. Following is a list of publications in the open literature. The proprietary information (patent and intellectual property) is reported in the next Section.

- Lee, D.-W. and M.-D. Cheng (2005) Particle generation by 266-nm laser ablation during surface decontamination, *Aerosol Science and Technology*, submitted in March.
- Lee, D.-W. and M.-D. Cheng (2005) Investigations of particles generated by 266-nm laser ablation during the surface decontamination, Congress on Optics and Laser Ablation, Calgary, Sept., 2005.
- M.-D. Cheng and D.-W. Lee (2005) Laser-Generated Airborne Particles during Surface Decontamination, European Aerosol Conference, Ghent, Belgium, August.
- Cheng, M.-D. and D.-W. Lee (2005) Investigation of Nanoparticle Formation during Surface Decontamination and Characterization by Pulsed Laser, Proceeding of American Chemical Society, Environmental Management Science Program, Accepted July.
- Lee, D.-W. and M.-D. Cheng (2004) Particle Generation by Laser Ablation during Surface Decontamination, *J. Aerosol Sci.*, 35:1527-1540.
- Lee, D.-W. and M.-D. Cheng (2004) Investigation of Nanoparticle Generation during Surface Decontamination by Laser Ablation at Low Fluence, *J. Aerosol Sci.*, 35:1513-1526.
- Li, W., D.-R. Chen, and M.-D. Cheng (2004) Development of a multiple-stage DMA, Presented at the AAAR Conference in Atlanta, GA in Oct..
- Chen, D.-R., D.-W. Lee and M.-D. Cheng (2004) Nanoparticle dynamics in laser ablation process, Presented at the AAAR Conference in Atlanta, GA in Oct..
- Lee, D.-W. and M.-D. Cheng (2004) Investigations of nanoparticle generation during the laser ablation decontamination, Presented at the AAAR Conference in Atlanta, GA in Oct.
- Cheng, M.-D. Cheng, D.-W. Lee, and B. Gu (2003) Investigation of nanoparticle formation during surface decontamination and characterization by pulsed laser, American Chemical Society/EMSP Proceeding, New York, NY.
- Lin, Y.-L. and M.-D. Cheng (2002) Removal of contaminants from target surfaces by laser ablation: formation of nanoparticles, presented at the Annual Meeting of AAAR.

Optional Proprietary Information: A **M**ultistage **D**ifferential **M**obility **A**rray (MDMA) was developed during the second year of the project by our Washington University subcontractor based on the initial idea developed jointly by Dr. Cheng (the lead PI) and Dr. Chen (the PI at Washington University). The prototype instrument was delivered in April, 2004, and tested throughout March 2005. The prototype was returned to Washington University in April, and is currently undergoing optimization and refinement. The MDMA was designed as a device capable of fast scanning using a flexible size ranging technology. A DOE intellectual property disclosure has been filed by ORNL and was issued on February 24, 2004 (1341, S-101,935). Preliminary data indicate that the instrument is capable of providing size distribution results on the order of seconds for particle sizes ranging from 10 to 250 nm, although the original design was for particles 2 nm and larger and the scanning time was supposed to be on the order of milliseconds. Calibration of the prototype unit shows superior performance compared to existing commercial models. New theory was also developed to explain the enhanced sizing performance of this multistage design of DMA.