DOE/OBER EMSP Project #82,807

Physico-Chemical Dynamics of Nanoparticle Formation during Laser Decontamination

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1. **Research Objective**: Laser-ablation based decontamination is a new and effective approach for simultaneous removal and characterization of contaminants from surfaces (e.g., building walls, ground floors, etc.). The scientific objectives of this research are to: (1) characterize particles generated during laser decontamination, (2) develop a technique for simultaneous cleaning and verification, and (3) develop a model for predicting particle generation. The research will provide fundamental data regarding the particle generation mechanisms, and a model for prediction of particle generation such that an effective control strategy can be devised to facilitate worker protection.

2. **Research Progress and Implications**: This report summarizes work performed from FY02-04. A technique for simultaneous surface cleaning using laser plasma and contaminant verification using the plasma emissions has been developed. The effects of laser treatment (ablation) on surface decontamination were systematically examined. The decontamination technique does not produce a large quantity of highly contaminated secondary liquid waste that could be produced when an alternative technique such as a wet scrubbing method is employed. The new technique will save both time and cost by preventing removal of an unnecessarily large quantity of material during building decommission and decontamination of DOE facilities. 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 three years, a large volume of experimental data has been collected at the Laboratories of Aerosol Science and Technology (ASTL) 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 research purposes. It will possibly take another year to fully analyze the data. However, previous analysis indicates that the particles produced during the decontamination/ablation process are ultrafine ($d_p < 100$ nm) and fine particles ($d_p < 1{,}000$ nm). Rarely, particles greater than 1 micrometer were found. These facts are unequivocal for all the materials tested. 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. A TEM image (Fig. 1) of the particles generated from alumina and the energy dispersive spectrum (EDS) of the particles (Fig. 2) are shown below. The main circle (~ 100 nm in diameter) was likely formed by condensation of Al vapor onto nuclei, because the particle surface appears to be coated with Al as indicated in the EDS.

The tails extending out of the circle are aggregates of small particles produced by the ablation. We did not observe any large supermicron size particles in this grid, which is consistent with other TEM samples and SMPS data.

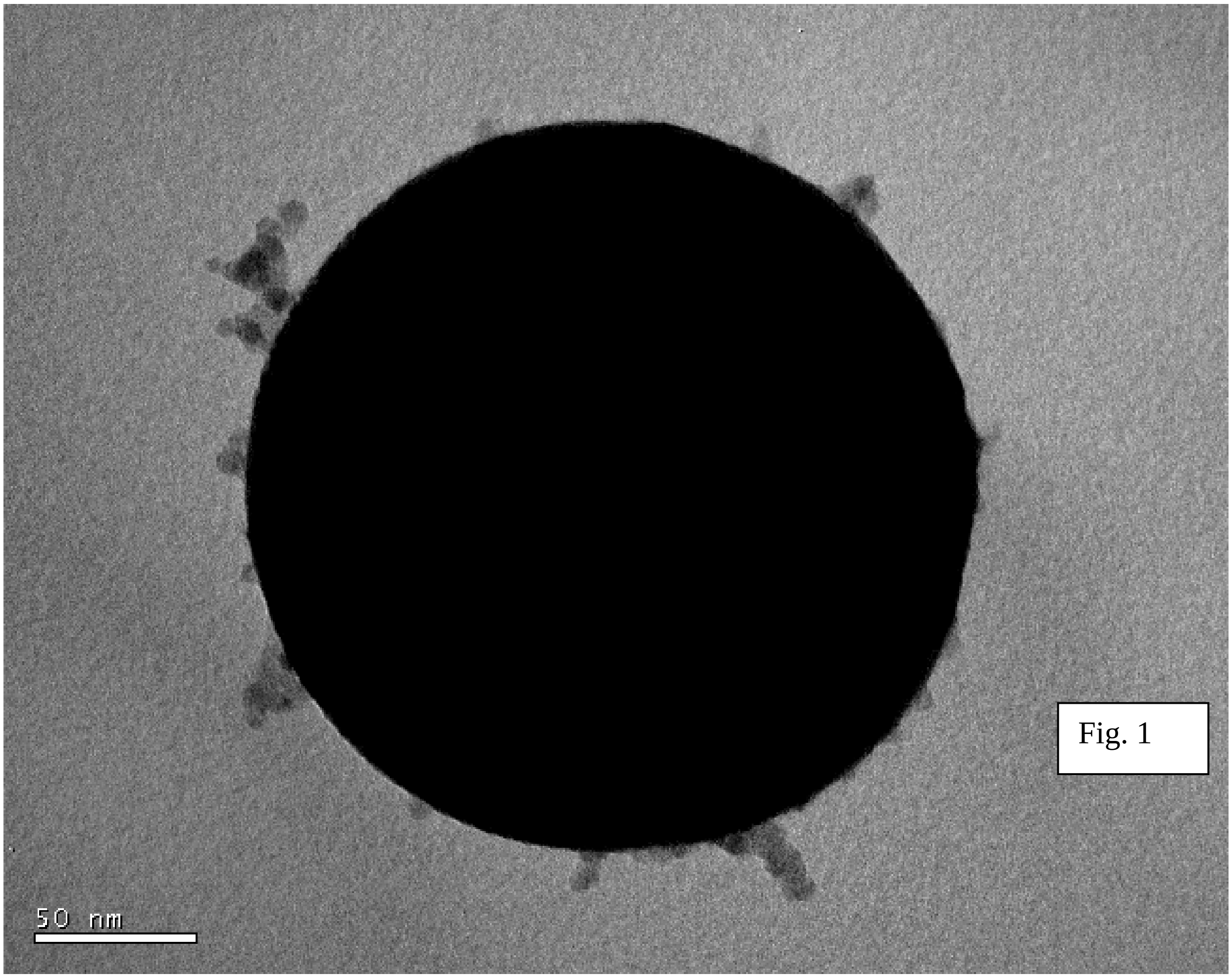
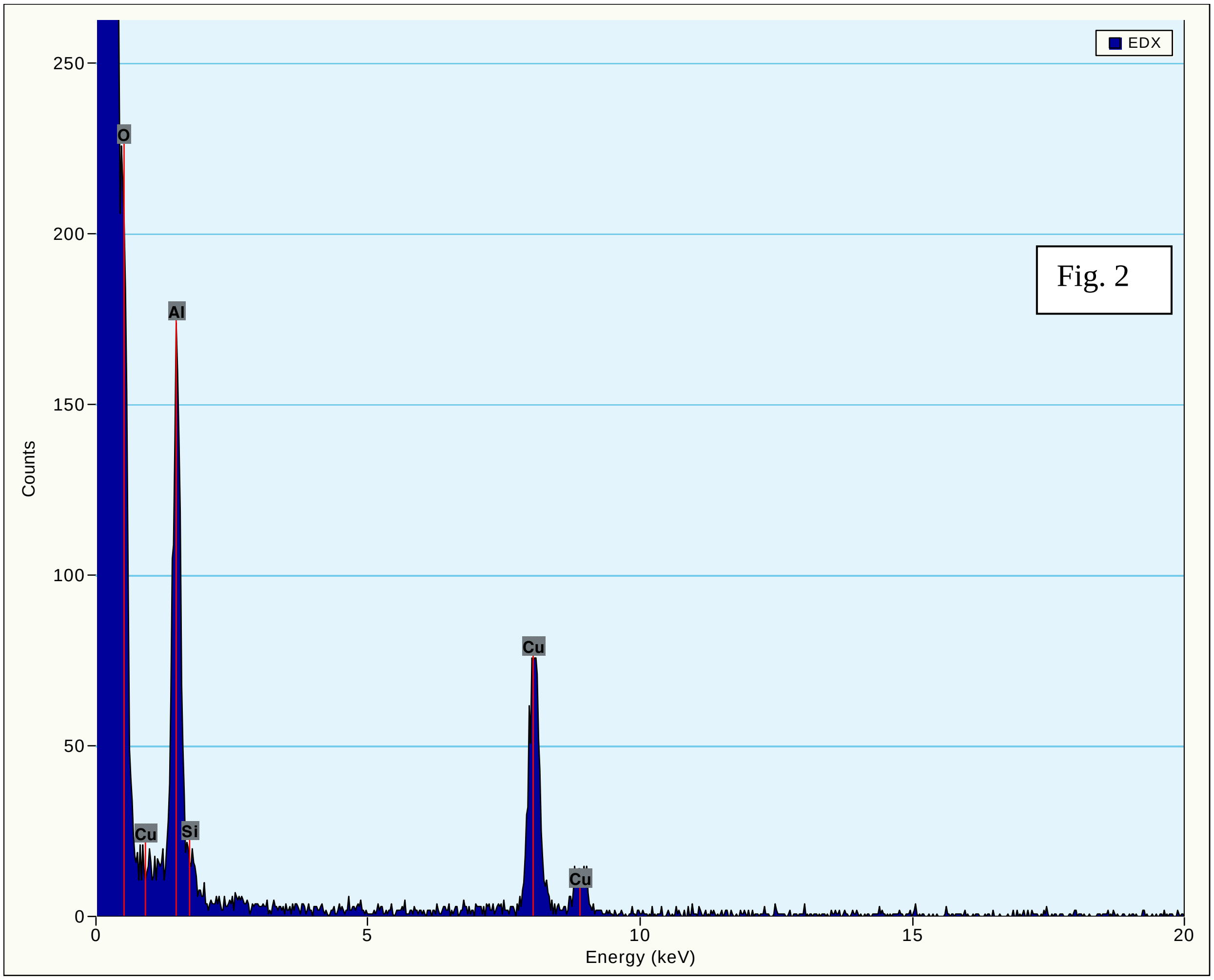


Fig. 1

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 a 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.

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. This result supports 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 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.

3. **Planned Activities**: This 3-year project will be completed by September 30, 2004, but we have a commitment from the EMSP program to continue working through the end of the fourth year (FY2005) with the planned activities including to (1) continue data analysis and model simulation, (2) publish and disseminate information about this work, (3) continue to pursue

technology transfer and patent the technologies developed in this project.

4. **Information Access**: The works we have performed during the past three years have started to bear fruit. Following is a list of publications in the open literature. The proprietary information (patent and intellectual property) is reported in the next Section.

- Removal of contaminants from target surfaces by laser ablation: formation of nanoparticles, Y.-L. Lin and M.-D. Cheng, presented at the Annual Meeting of American Association for Aerosol Research, 2002.
- Investigations of nanoparticle generation during surface decontamination by laser ablation at low fluence, D.-W. Lee and M.-D. Cheng, J. Aerosol Science, in review, 2004.
- Investigations of nanoparticle generation during surface decontamination by laser ablation at high fluence, D.-W. Lee and M.-D. Cheng, J. Aerosol Science, in review, 2004.
- Investigation of nanoparticle formation during surface decontamination and characterization by pulsed laser, M.-D. Cheng, D.-W. Lee, and B. Gu, American Chemical Society/EMSP Proceeding, New York, NY, 2003.
- Study of laser generated air contaminants and control, M.-D. Cheng, J. Laser Application, in review, 2004.
- Development of a multiple-stage DMA, W. Li, D.-R. Chen, and M.-D. Cheng, to be presented at the AAAR Conference in Atlanta, GA in Oct. 2004.
- Nanoparticle dynamics in laser ablation process, D.-R. Chen, D.-W. Lee and M.-D. Cheng, to be presented at the AAAR Conference in Atlanta, GA in Oct. 2004.
- Investigations of nanoparticle generation during the laser ablation decontamination, D.-W. Lee and M.-D. Cheng, to be presented at the AAAR Conference in Atlanta, GA in Oct. 2004.

5. **Optional Proprietary Information**: A **S**tackable **D**ifferential **M**obility **A**rray (SDMA) was developed during the second year of the project by our Washington University subcontractor. The prototype instrument was delivered in April, 2004, and is currently undergoing testing at ASTL at Oak Ridge National Laboratory (ORNL). The SDMA 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. Design for the first stage in the SDMA will have to be redone to eliminate the turbulence when operating at high flow rate. Calibration for the transfer functions of the stages in the prototype SDMA is also ongoing.