Environmental Management Science Program Progress Report

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Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation
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Research Objective: Laser ablation is being studied as a method both for removing and for measuring contaminated surface layers from concrete. The objectives of this research are to determine the mechanism and efficacy of laser ablation, to understand the chemistry of contaminated concrete surfaces, and to chemically and physically characterize the captured ablation effluent, which would become the stored waste. The method is attractive because it adds no additional waste, offers fine control over the amount of material removed, can work on cracked, curved or irregular surfaces, and can potentially be instrumented for real-time contamination analysis. While the focus of this project is on concrete, the technology should be applicable to any surface requiring contaminant removal.

Research Progress and Implications: This report summarizes work after 28 months of a three-year project. Concrete surfaces were ablated with an industrial pulsed Nd:YAG laser delivered via a fiber optic cable. The virgin and ablated surfaces and ablation effluent were chemically and physically characterized. In addition, optical emission spectra were obtained on-line during the laser ablation process itself.

We have shown that several different ablation mechanisms exist simultaneously when concrete is ablated at high power with a pulsed laser. The most important is the thermal shock created by the laser pulse. Rapid thermal expansion of a small volume of material causes stress to build up between the hot surface and cold bulk. When the thermally induced stress exceeds the tensile strength the material fractures into small pieces (up to a few millimeters in diameter) and explodes off the surface. This mechanism is particularly important in the aggregate portion of the concrete (i.e. sand and rocks) which typically makes up about 90% of the bulk of high density concrete, so that the overall material removal rate is dominated by this process. The ablation rate depends on several factors, most importantly laser power, but also pulse repetition rate, raster rate, focused spot diameter, and focal position with respect to the surface. In general, high power, fast raster rates and large beam diameters lead to the highest removal rates. The ablation efficiency, defined as mass removed per unit energy delivered to the surface, is unaffected by parameters such as total power or focused spot size. In particular, we have demonstrated that the ablation efficiency doesn't change over a wide range of irradiances (power per unit area). This is important for two reasons. First, concrete ablation with continuous wave lasers is critically sensitive to irradiance, and therefore more difficult to control and extrapolate from one laser

system to another. Second, it shows that the pulsed laser process is scalable to lasers of arbitrary energy, since the laser spot size can always be easily adjusted to keep the irradiance within the wide bounds determined by this study. Hence the ablation rate scales only with the total laser power. This finding makes it possible to predict concrete ablation rates for any Nd:YAG laser system with pulse lengths similar to those used in our study, i.e. 0.5 to 1 ms.

We have found that efficiency drops at slow raster rates where consecutive pulses overlap significantly, leading to melting rather than ablation of the material. In this case the system behaves more like a continuous wave laser which glazes the surface as it passes over it. Excessive pulse overlap reduces the ablation efficiency in several ways. First, laser energy that would otherwise have been used to remove material is instead wasted in the energy-intensive phase transition required to melt the material. Second, the glazed surface is more reflective, resulting in reduced absorption of the laser energy in the overlapped region. Finally, residual heat left in the concrete from previous pulses reduces the thermal gradient induced by the overlapping pulse, thereby reducing the magnitude of the thermal shock.

The cement portion of the concrete comprises only about 10% of the total, but is important because it is the phase in which the bulk of the contamination resides in concrete that has been exposed to water-born radionuclide ions such as Cs and Sr. The cement phase can melt, spatter, vaporize, and/or disaggregate (i.e. explode) depending on the intensity and duration of the laser pulse. The laser-melted or -vaporized cement forms an aerosol that can have a very different chemical composition than the virgin cement. The aerosol particle size distribution is bimodal, with peaks at the high (8.5 μm) and low (<0.5 μm) ends and a minimum at about 1 μm. This suggests that particles form by two mechanisms, namely vaporization/condensation for small particles and melt/spatter for large particles. This interpretation is bolstered by energy dispersive x-ray spectroscopy, which showed that small particles had disproportionately large concentrations of aluminum compared to both the larger particles and the virgin cement. This suggests that small particles form by condensation from vapor, with an aluminum-rich nucleating phase. Neutron activation analysis (NAA) showed that cesium and strontium concentrations in the aerosol were also strongly correlated with particle size. Particles with aerodynamic diameters below 0.5 μm were enriched in cesium by up to a factor of two compared to the virgin cement, while larger particles were substantially depleted in cesium. In contrast, particles in the aerodynamic size range from 0.5 to 1.6 μm - the smallest of those formed by melt/spatter - were enriched in strontium by up to a factor of two over the virgin cement, while all others were depleted. The NAA data is consistent with the proposed particle formation mechanisms. Since cesium is very volatile compared to the other elements in the cement, it should be distilled out of the melted material and appear in the particles formed from the vapor phase. Strontium is less volatile and tends to remain with the melted/spattered fraction, though the reason for its preferential precipitation in the smaller of the melted particles is unclear.

Laser desorption mass spectrometry (LDMS) of cesium- and strontium-doped Portland cement and high density concrete samples showed that cesium resides in the adsorbed water in the cement pores, while strontium resided in the cement matrix itself. These results support the interpretation of the chemical fractionation observed in the ablation aerosol. LDMS analysis of ablated samples also demonstrated the potential for decontamination by laser ablation. A sample of the exterior surface of high density concrete exposed to an aqueous solution of CsCl was shown to have a 30- to 300-fold reduction of Cs after removal of 0.6 to 0.8 mm of material after a single high-power laser ablation pass.

Optical emission spectra of the ablation plume were collected and analyzed. A number of peaks were assigned to Cs and Sr, as well as many of the cement matrix elements. The high

power and long pulse duration of the industrial Nd:YAG make it especially well suited to this type of analysis and offer the possibility of on-line analysis for a number of elements.

Planned Activities: Laser ablation studies will be extended to higher powers and the effect of varying pulse durations will be investigated. We will also compare the performance of Nd:YAG and CO_2 lasers to assess the effect of wavelength on the ablation efficiency and mechanisms. We will continue to investigate the use of laser-induced breakdown spectroscopy in this application as an on-line contaminant analysis tool.