Pulsed Laser Ablation of Cement and Concrete

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Abstract

Laser ablation was investigated as a means of removing radioactive contaminants from the surface and near-surface regions of concrete from nuclear facilities. We present the results of ablation tests on cement and concrete samples using a pulsed Nd:YAG laser with fiber optic beam delivery. The laser-surface interaction was studied on model systems consisting of Type I Portland cement with varying amounts of either fine silica or sand in an effort to understand the effect of substrate composition on ablation rates and mechanisms. The neat cement matrix melts and vaporizes when little or no sand or aggregate is present, and energy dispersive X-ray spectroscopy showed that some chemical segregation occurs in the effluent of ablated cement. The presence of sand and aggregate particles causes the material to fracture and disaggregate on ablation, with particles on the millimeter size scale leaving the surface.

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Introduction

The waste stream generated in the decontamination and decommissioning of nuclear facilities includes a significant volume of material that is contaminated only in the surface or near surface region. Removal of the contaminated layer would greatly reduce the volume of radioactive waste requiring storage. The US Department of Energy and others engaged in the decontamination and decommissioning of nuclear facilities may realize a significant cost benefit if this surface material is analyzed and separated from the uncontaminated bulk material.

Lasers have been investigated previously as a means of removing layers from cement and concrete surfaces[1-4]. A high intensity pulsed laser beam delivered via a fiber optic cable can ablate concrete surfaces and the resulting effluent, consisting of aerosol and disaggregated particles, could be efficiently collected with a vacuum shroud and filtration system and analyzed for contaminants on-line via mass spectrometry or atomic emission spectroscopy. This study was undertaken to determine the mechanism and efficacy of laser ablation in removing contaminated surface layers, and to chemically and physically characterize the captured ablation effluent which would become the stored waste. This paper concentrates on the effects of ablation on the cement phase of concrete, since this is where the contaminant ions reside.

Experimental

Samples were cast in the laboratory using Type I Portland cement and either fine silica (300 µm particle size) or silica sand (0.5 - 1 mm diameter) at levels ranging from 0 to 60%. The water/cement ratio was 0.5. Samples were cured at room temp for at least 30 days prior to ablation.

Laser ablation experiments were done with the 1064 nm fundamental of an Electrox 1.6 kW pulsed Nd:YAG laser. A schematic of the ablation system is shown in Figure 1. The beam was delivered via a fiber optic cable and focused to a 0.55 mm spot via a 120 mm lens. The typical free-running Nd:YAG energy delivered was 2 J per pulse at a pulse length of 0.5 ms and repetition rate of 800 Hz. The sample stage was moved under the stationary beam at a rate of 45 cm/s, giving an ovular ablation spot as depicted in Figure 2. The linear pulse overlap was 27%, the area of overlap was 9% (see Figure 2). The depth and width of the ablated tracks were measured with a Nikon SMZ-2T stereo microscope. The ablation effluent was captured either on a 0.2 μm Nucleopore filter or with a multi-stage impactor. The effluent was analyzed via scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

Results and Discussion

Samples of Type I Portland cement containing 20% fine (300 μm) silica melted, flowed, and vaporized when ablated with the Nd:YAG laser. Figure 3 is an electron micrograph of several ablation tracks in the material, and shows considerable melting and flow, especially in the region where the laser was slowed to a halt (lower right of Figure 3), resulting in many overlapped pulses. The tracks are roughly the same width as the focussed beam, ~0.6 mm, and are ~0.5 mm deep. Figure 4 is a high magnification micrograph of the interior of an ablated track, and shows melting and foaming of the cement matrix, along with a fractured silica grain (flat angular feature underlying the large sphere in Figure 4). In addition, spheres of melted/resolidified cement in sizes ranging from sub-micron to 20 μm are seen in this micrograph. The spheres were also seen in micrographs of the virgin surface, indicating some spatter of the ablated material back onto the surface. Figure 5 is a micrograph of the ablation effluent collected on a filter, and shows a range of fine particles in the size range from sub-micron to a few tens of microns. Many of the large spheres appear to be hollow, as evidenced

by holes and dimples, while the smaller ones appear to be solid. There are also some small irregular chunks of material.

The laser-surface interaction in these samples takes the form of heating, melting, spatter, and vaporization. The foamy appearance of the ablated surface in Figure 4 is due to the melting and rapid dehydration of the cement. The cement matrix typically contains ~5% of labile water, and another 20-30% of water of hydration. The rapid release of this water at high temperature results in a steam explosion which propels the bulk of the effluent away from the surface and accounts for the observed structure of both the foamy surface and the hollow spheres. Only the smallest spheres appear to be solid, indicating perhaps that these particles formed from material that vaporized and condensed. This conclusion is supported by EDX spectra (see below).

When the filler was changed from fine silica to coarse silica sand with a particle size comparable to the focussed beam diameter (0.5 - 1 mm), the ablation mechanism became more complex. In addition to the fine aerosol particles, a considerable amount of fractured and dislodged material was produced. Figure 6 is an optical micrograph of the effluent from a sample containing 60% sand, and shows fractured sand particles and dislodged chunks of cement in a size range up to a few hundred microns. This material was not swept into the impactor system, but was collected from the surface of the sample stage. The impactor collected the fine aerosol as before, along with irregular chunky particles up to 200 µm in diameter. The results indicate that the energy deposited in the sand particles results not in melting, as is the case in the cement matrix, but in rapid heating and thermal shock that fractures the particle. The resulting shock wave disaggregates and dislodges portions of the cement matrix, resulting in the irregular chunks of material in the effluent observed in Figure 6.

Figure 7 shows the ablation rate as a function of the sand or fine silica content. In general ablation rates rise as the filler content increases, however the samples filled with sand ablated faster than those filled with the same amount of fine silica. Samples containing 40% fine silica were ablated at a rate of 0.10 cm^3/s, compared to 0.084 cm^3/s for the neat Portland cement. However, when the filler was 40% coarse sand the ablation rate 0.12 cm^3/s. The difference in ablation rates can be ascribed to the difference in ablation mechanisms. The dominant ablation mechanism of neat cement and cement with fine silica was spatter and vaporization. The resulting ablation plume of vapor and aerosol above the laser spot is not completely transparent to the beam[5]. Laser heating converts the plume to an optically dense plasma that partially absorbs, refracts, and reflects the beam. Thus, a significant fraction of the laser energy is lost, and the ablation rate is lower as the result of the decreased laser-surface coupling. The high ablation rate in the case of the sand-filled material may derive from the fact that the coarse sand particles are fractured and dislodged from the matrix before reaching their melting or vaporization points. The laser energy is used more efficiently in this case since no phase transition is involved. The amount of vapor and fine aerosol in the ablation plume is reduced, resulting in less attenuation of the incoming beam via the mechanisms listed above, however the coarse chunks should scatter a portion of the incoming beam and reduce the total energy delivered to the surface. The relative attenuation factors for the two mechanisms is unknown.

While adding sand enhanced the ablation rate by introducing a new mechanism, it did not completely eliminate the melting and vaporization of the cement matrix. Figure 8 compares the size distributions for aerosols collected by the impactor from ablation of cement containing from 20 to 60% sand. SEM confirmed that the impactor collects only the aerosol particles and rejects the fractured and dislodged material; therefore it samples only that fraction of the effluent produced as a result of spatter or vaporization of the cement matrix. Figure 8 shows that the size distributions are nearly identical, indicating that fracture/disaggregation and

spatter/vaporization co-exist as mechanisms of ablation when sand is present. This finding is important in light of the fact that some radionuclides such as americium and plutonium disperse themselves in the cement matrix, while others such as cesium reside at the interfaces between the matrix and aggregate particles[6]. This effect, coupled with the plurality of ablation mechanisms, could result in the resegregation of contaminants within the laser ablation effluent.

EDX spectra of the ablation effluent from the Portland cement samples filled with sand confirmed that both the larger (hollow) aerosol particles and the chunky material were identical in composition to the virgin cement, while the angular, fractured grains were silica. An interesting trend was noted in the EDX spectra of small solid spheres however; in general, smaller spheres were richer in aluminum. For example, the aluminum content of 5 µm spheres was 7.5%, while that of 15 µm spheres was 4.6%. The aluminum content of the Type I Portland cement before ablation was 2.5%. The most likely explanation for the correlation of aluminum content with particle size is that the solid shperes are formed by condensation from the vapor, with the nucleating phase being rich in aluminum.

Portland cement is a complex material containing many distinct chemical phases. The principle phases are hydrated calcium silicates, while the second most abundant are hydrated calcium aluminates [7]. Since the EDX technique probes to a depth of ~1 µm, the spectra show only the near-surface region of the spheres. If the solid spheres were formed by vaporization and condensation, probing smaller and smaller spheres is similar to performing a depth profile of one large sphere. The aluminum concentration rises as one approaches the heart of a sphere, indicating that an alumina or aluminate phase is responsible for nucleation. This finding is significant in light of literature showing that Cs ion, a common radionuclide contaminant, binds preferentially to alumina and aluminum-rich phases[8,9]. This could lead to a segregation of contaminants within the effluent, with cesium concentrated in the smallest particles.

Conclusions

Pulsed laser ablation of cement and concrete produces greatly varying effluents and ablation rates depending on the age and composition of the material. The cement matrix melts, dehydrates, and vaporizes when ablated with a high-power pulsed Nd:YAG laser, while sand and aggregate material tends to fracture and dislodge without melting. The aerosol produced from the cement matrix consists of particles similar in chemical composition to the original cement, with the exception that the smaller aerosol particles tend to be enriched in aluminum, owing to nucleation by an alumina or aluminate phase.

Acknowledgement

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Figure Captions

Figure 1. Schematic drawing of the laser ablation system.

Figure 2. Depiction of the pulse overlap. Sample travel under the circular beam during the 0.5 ms pulse results in an ovular ablation spot. The area of overlap was calculated by integrating the region of intersection and dividing by the area of an oval.

Figure 3. Low magnification scanning electron micrograph of ablation tracks in a Portland cement sample containing 20% fine silica (300 µm). The bar length is 2 mm.

Figure 4. High magnification scanning electron micrograph of an ablated Portland cement surface. The bar length is 50 µm.

Figure 5. Scanning electron micrograph of the aerosol resulting from the laser ablation of a Portland cement sample containing 20% fine silica (300 µm). The field of view is 150 µm.

Figure 6. Optical micrograph of fractured material resulting from the laser ablation of a Portland cement sample containing 60% sand.

Figure 7. Laser ablation rate as a function of fine silica or coarse sand content.

Figure 8. Particle size distributions obtained from impactor analysis of the aerosol portion of the effluent from the laser ablation of cement samples containing 20, 40, and 60% sand.

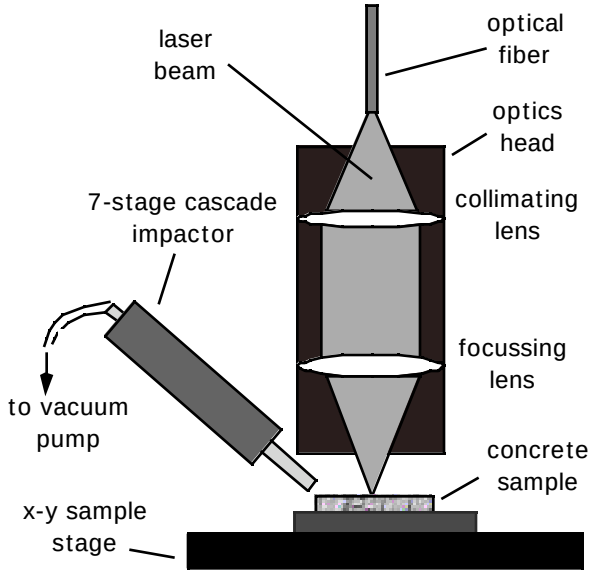

Figure 1

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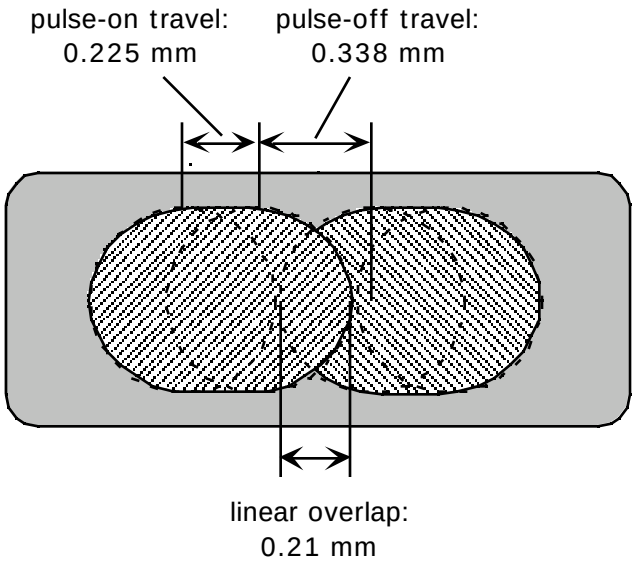

Figure 2

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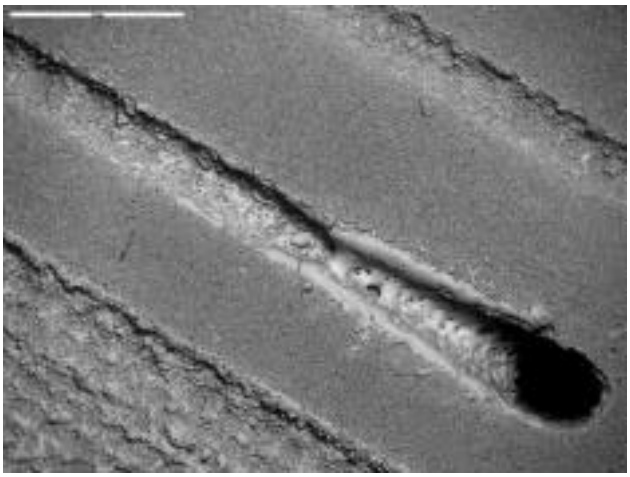

Figure 3

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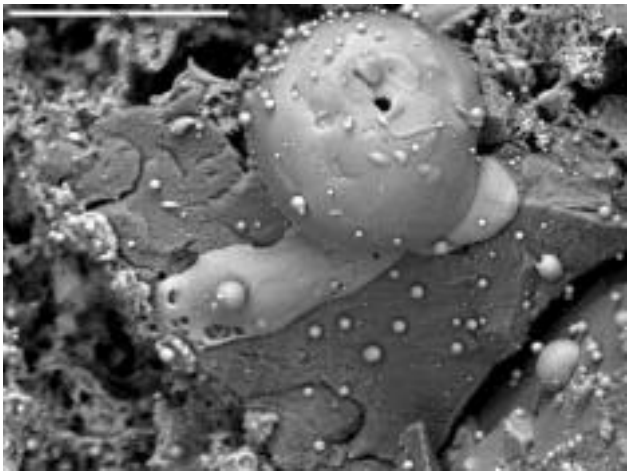

Figure 4

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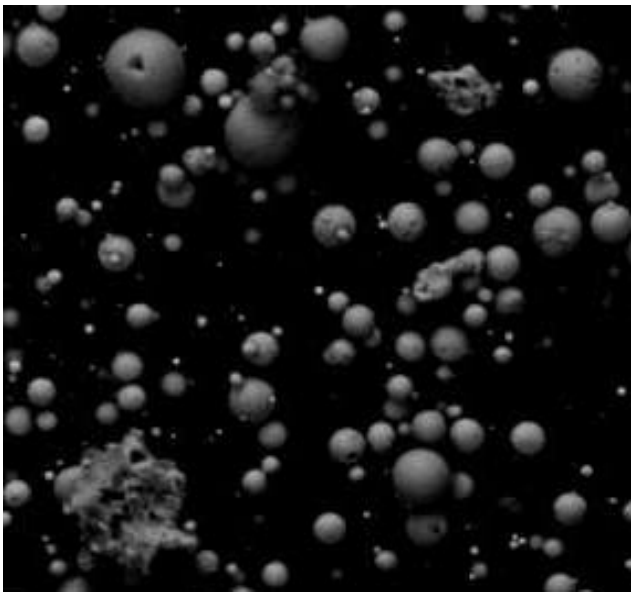

Figure 5

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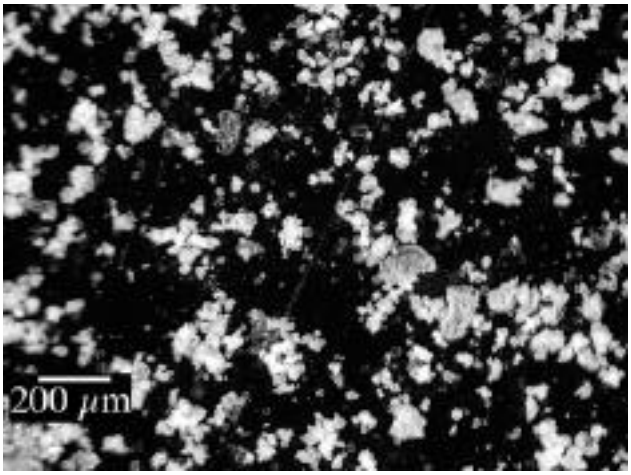

Figure 6

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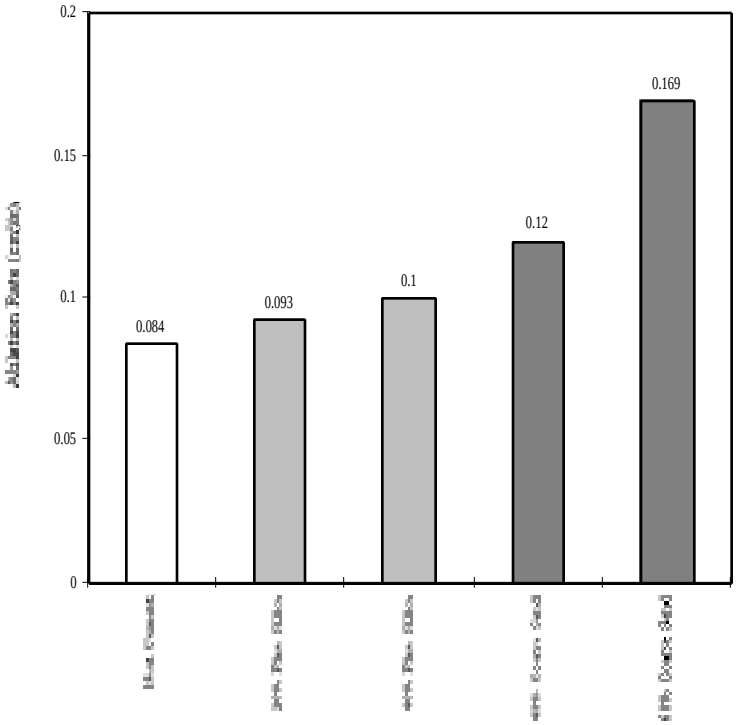

Figure 7

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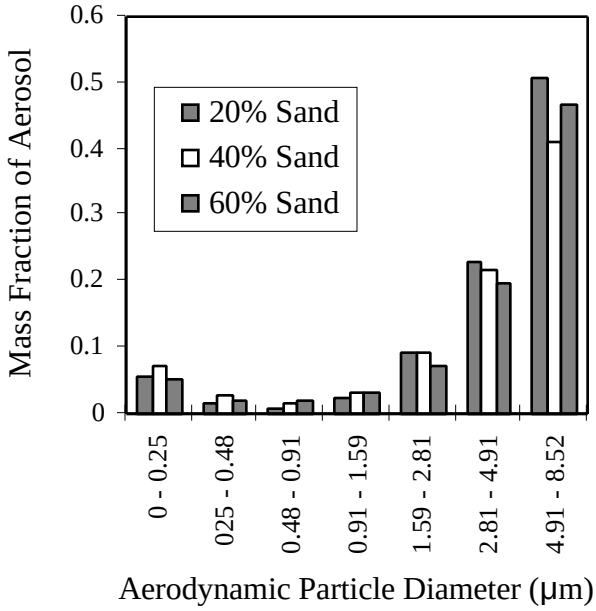

Figure 8

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