



Measurement of chlorine concentration on steel surfaces via fiber-optic laser-induced breakdown spectroscopy in double-pulse configuration

X. Xiao^{a, b}, S. Le Berre^b, D.G. Fobar^a, M. Burger^{a, d}, P.J. Skrodzki^{a, d}, K.C. Hartig^{b, c}, A.T. Motta^b, I. Jovanovic^{a, d, *}

^a Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI 48109, United States

^b Department of Mechanical and Nuclear Engineering, The Pennsylvania State University, University Park, PA 16802, United States

^c Nuclear Engineering Program, University of Florida, Gainesville, FL 32611, United States

^d Center for Ultrafast Optical Science, University of Michigan, Ann Arbor, MI 48109, United States

ARTICLE INFO

Article history:

Received 6 October 2017

Received in revised form 10 January 2018

Accepted 11 January 2018

Available online xxxx

Keywords:

Laser-induced breakdown spectroscopy (LIBS)
Optical fiber
Remote inspection
Double pulse
Chlorine

ABSTRACT

The corrosive environment provided by chlorine ions on the welds of stainless steel dry cask storage canisters for used nuclear fuel may contribute to the occurrence of stress corrosion cracking. We demonstrate the use of fiber-optic laser-induced breakdown spectroscopy (FOLIBS) in the double-pulse (DP) configuration for high-sensitivity, remote measurement of the surface concentrations of chlorine compatible in constrained space and challenging environment characteristic for dry cask storage systems. Chlorine surface concentrations as low as 5 mg/m² have been detected and quantified by use of a laboratory-based and a fieldable DP FOLIBS setup with the calibration curve approach. The compact final optics assembly in the fieldable setup is interfaced via two 25-m long optical fibers for high-power laser pulse delivery and plasma emission collection and can be readily integrated into a multi-sensor robotic delivery system for *in-situ* inspection of dry cask storage systems.

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1. Introduction

The extended usage of the dry cask storage systems (DCSS) that results from the delay in opening of a permanent geological repository for used nuclear fuel has raised serious concerns about the overall structural integrity of DCSS [1–3]. Remote inspection of DCSS that comprises a stainless steel canister and concrete overpack is desired, which motivates the development of a multi-sensor robotic inspection system for such purpose. One example of an effort that could lead to accurate and comprehensive inspections is development of the Portable Robotic Inspection of Nuclear Storage Enclosures (PRINSE) system [4]. Stress corrosion cracking (SCC) has been considered to be the most likely degradation mechanism of steel canisters at marine sites. The accumulation of chlorine (Cl) anions in the deliquescent airborne sea salt particles deposited on the heat affected zones of the welding lines over a long service life may provide sufficient Cl, as well as susceptible materials and tensile thermal stresses that are responsible for SCC [5,6]. According to a field

test conducted in Japan, the typical Cl concentration observed on the steel canister is in the range of 1–100 mg/m² [7]. Although the concentration may be significantly affected by the environmental conditions [6], we targeted this Cl surface concentration range in our study.

Laser-induced breakdown spectroscopy (LIBS) has proven to be an effective approach for detection of Cl attached to stainless steel surfaces [8,9]. However, the sensitivity of the Cl concentration measurement via LIBS is limited by the high ionization potential of Cl and by the difficulty in populating the relatively high upper level energy of neutral chlorine for the transition of interest. This is especially the case when high-power laser pulses need to be delivered by flexible fiber optics through the duct of the air ventilation system of DCSS. In this situation, the maximum laser irradiance that can be achieved at the sample surface is limited by multiple factors related to the optical fiber, including its aperture, laser coupling efficiency, optical damage threshold, intermodal dispersion, and the focusing conditions that can be practically realized post fiber exit. Fiber-optic laser-induced breakdown spectroscopy (FOLIBS), ever since its emergence, has been successfully applied to a number of “real-world” applications that require remote *in-situ* analysis; however, in none of them there was special attention paid to the halogen Cl,

* Corresponding author at: Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI 48109, United States.
E-mail address: ijov@umich.edu (I. Jovanovic).

which is difficult to detect through its optical emission [10–15]. In recent work, Eto and Fujii [9] demonstrated the potential to detect Cl emissions in FOLIBS at Cl surface concentrations of approximately 50 mg/m². However, reliable detection of the most intense Cl I emission line (837.6 nm) under typical LIBS ablation conditions and located outside the vacuum ultraviolet region remains challenging when quantitative measurements of Cl on steel surfaces are sought at even lower concentrations. Efforts were undertaken to improve the sensitivity of Cl measurement by detecting alkali metals as surrogates for Cl [16]. However, this measurement could become inaccurate if Cl speciation occurred during the transport of salt in the environment, such that the ratio of concentrations of alkali metals to Cl could be modified [6]. Direct Cl measurement in FOLIBS is therefore motivated to a significant extent by the desire to overcome the limitations of the surrogate measurements. Special approaches, such as the use of helium buffer gas [17], additional excitation by electrical discharge [18], and double-pulse (DP) excitation technique [19], can be explored to improve the sensitivity and accuracy of direct Cl measurement in FOLIBS. From those approaches, the DP excitation technique appears most suitable for use in the DCSS environment.

DP excitation is expected to significantly enhance the characteristic emissions from the plasma through a reheating process by a second laser pulse, such that denser and hotter plasma can be formed, containing a large population of analyte atoms that are sufficiently excited to contribute to the desired Cl I 837.6 nm emission line [20]. Extensive laboratory studies of detection of Cl using DP LIBS have demonstrated the effect of the use of a second laser pulse by varying its wavelength, energy, and inter-pulse delay in orthogonal geometry [17,21]. Labutin *et al.* first explored the possibility of using DP technique in a more practical collinear configuration to assist the excitation of Cl atoms, and observed prominent enhancement of the analytical Cl I line at 837.6 nm using a DP approach in their laboratory study [19]. A limit of detection (LOD) for chlorine of 50 ppm in concrete was achieved by using an internal standard of the Mg II line at 279.08 nm. Additionally, a mobile system, equipped with an air-cooled Q-switched Nd:YAG laser (1064 nm), a compact Czerny–Turner spectrometer, and an ungated CCD camera was also developed by this group, achieving an LOD of 1500 ppm for Cl. The aim was *in-situ* quantification of corrosive active non-metals under ambient conditions in concrete, and represents a promising way for probing for presence of Cl in the field [22]. It should be noted that none of these prior studies incorporated optical fibers for high-power laser pulse delivery, such as in FOLIBS. Another obvious advantage of using DP in FOLIBS is simply that more energy can be delivered onto the target when splitting a single pulse into two separate pulses that are delayed with respect to each other while propagating through the optical fiber.

In this study, a collinear DP configuration was adopted in FOLIBS to enable the observation of the Cl I emission line at 837.6 nm on the steel surface under ambient conditions, with a goal to achieve sensitivity to lower Cl concentrations. Two DP FOLIBS setups have been developed and tested. The first setup enables the study of the feasibility of DP FOLIBS for direct Cl detection in laboratory conditions, while the second has been designed to be more compact, aiming to fulfill the practical requirements of the remote inspection of DCSS. Standard samples for conventional LIBS calibration curve approach were prepared on steel substrates using a nebulizer-based process developed for our prior surrogate measurements [16]. No aggregation and crystallization of salt aerosols was observed on the sample surfaces with scanning electron microscopy (SEM). The surface concentration of Cl on the prepared samples is in the range of 1–100 mg/m², calculated on the basis of deposition parameters and further confirmed by ion chromatography (IC). It is demonstrated in this study that the DP FOLIBS approach, which is fully compatible with integration into a robotic delivery system such as PRINSE [4,23], can detect Cl on stainless steel surfaces with sufficiently high sensitivity to meet the most demanding targets of DCSS inspection.

2. Experimental setup and methods

2.1. Sample preparation

To benchmark the LIBS measurement, the standard samples were prepared through the use of PerkinElmer Mira-mist nebulizer (P/N N0775330), which produces a fine mist when delivering the synthetic seawater solution (ASTM D1141-98, Lake Products Company LLC), which interacts with an argon gas stream. The volumetric flow rate of the nebulizer was calibrated to be 0.25 mL/min, and the diameter of the spraying area was measured to be 4.5 cm when the nebulizer was kept 15 cm above the substrate. The stainless steel substrates were preheated by a Thermo Scientific Cimarec hot plate to 500 °C to provide near-instantaneous vaporization of water on contact with the heated surfaces, and helped avoid the aggregation of aerosol particles and formation of salt crystals, as can be seen under SEM measurement in our previous work [16]. This resulted in more homogeneous salt deposition relative to the unheated case. In order to prevent significant cooling down of the substrates during spraying, the selected dilution factor of 1/100 limited the exposure time of the substrates to less than 1 min. The Cl surface concentrations of the samples were calculated from the mass concentration of Cl in the diluted seawater solution, the flow rate of the nebulizer, the exposure time of the samples, and the sprayed area. The absolute surface concentrations of Cl on samples were further validated by IC (ICS 2500, Dionex Corp.), which is able to quantify Cl anions down to ~20 ppb when the salt depositions were washed off from the sample surfaces and dissolved in deionized water.

2.2. Laboratory DP FOLIBS setup

In the laboratory DP FOLIBS setup shown in Fig. 1, a Q-switched Nd:YAG laser (Quanta-Ray PRO-250-10, Spectra Physics) with pulse duration of ~10 ns and a repetition rate of 10 Hz was operated at its fundamental wavelength of 1064 nm. The beam diameter was first reduced using a Galilean telescope, and then the pulse was split using a plate beamsplitter. With this configuration, the path of one of the resulting pulses was increased by 12 m with respect to the other path, resulting in an inter-pulse delay of 40 ns, when the pulses were recombined by means of two half-wave plates and a polarizing beamsplitter. A similar DP scheme is commonly seen in femtosecond DP LIBS [24,25], in which the maximum enhancement effect is usually found when the inter-pulse delay is on the order of picoseconds [20,26]. However, the physical processes involved in the nanosecond laser-material interaction are known to differ significantly from those that occur when nanosecond lasers are used, such that the timescale of the plasma evolution may be very different [26]. Despite the fact that an inter-pulse delay on the order of magnitude of microseconds generally yields the strongest plasma enhancement in nanosecond DP LIBS [20,26], it is not practical to split a single laser pulse and provide the required hundreds of meters of optical delay for one of the pulses.

The DP sequence was coupled into the 10-m long optical fiber (Thorlabs FT1000EMT, 1-mm core diameter, NA = 0.39) using a plano-convex lens with a focal length of 300 mm. The input end face of the fiber was positioned slightly beyond the focus of the 300-mm lens to prevent fiber damage. Despite the lower coupling efficiency to the sample during ablation with the single pulse [27], the usage of IR wavelengths in DP configuration provided: (i) lower probability of damaging the fiber using 1.17 eV (1064 nm, fundamental wavelength of the Nd:YAG laser) photons compared to higher harmonics, such as 532 nm (second harmonic of the Nd:YAG laser); (ii) greater overall energy throughput; and (iii) strong plasma absorption of the second pulse, leading to enhancement of emission signal.

Two tight-focusing plano-convex lenses (30 mm focal length) were used to collimate the highly divergent DP sequence from the

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