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Robotic delivery of laser-induced breakdown spectroscopy for sensitive chlorine measurement in dry cask storage systems

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ABSTRACT

Chlorine-induced stress corrosion cracking is a degradation mechanism of concern for dry storage of used nuclear fuel. Remote detection of chlorine deposited on the stainless steel canister surface presents a challenge, since no direct line-of-sight is available. We demonstrate the design and use of double-pulse laser-induced breakdown spectroscopy installed on a robotic system for remote detection and measurement of the canister surface chlorine concentration. The system meets the stringent requirements of dry cask storage inspection environment, especially the constrained space. The externally located pulsed laser, spectroscopic instrumentation, and data acquisition setup were interfaced to a robotic delivery car using a pair of 25-m long optical fibers. We discuss the design and construction details of the chlorine detection system and its detection performance in both laboratory and field-deployable configurations. We show that chlorine concentrations as low as 10 mg/m^2 can be measured in field-compatible operations.

1. Introduction

Until geological disposal of spent nuclear fuel becomes available, spent nuclear fuel is stored on site in dry storage facilities, in which the spent fuel assemblies are enclosed in stainless steel canisters within a concrete overpack. Due to the unavailability of final disposal, the expected residence times of spent fuel in dry storage could be much longer than previously expected. This raises the possibility that slow developing degradation mechanisms could become of concern. One of these mechanisms is stress corrosion cracking of the metal in a marine environment, where salt deposition on the canister surface could assist crack propagation (Chu, 2013; Bryan and Enos, 2015). Thus it is necessary to assess the amount of salt (or chlorine) present on the surface of the canister after a long period of storage. It is highly desirable that such a measurement be performed remotely, in order to minimize the cost and time needed for inspection.

In this work we present a method for the direct measurement of chlorine (Cl) concentration levels on stainless-steel using a laser-induced breakdown spectroscopy (LIBS) (Miziolek et al., 2006; Noll, 2012; Cremers and Radziemski, 2013) system, which is fully integrated into a multi-sensor inspection system. LIBS is based on the principle that when a focused laser pulse of sufficient intensity strikes a target, a small surface layer of the material is ablated and ionized, forming a fast expanding plasma. During the relaxation of this plasma, ions, atoms, and/or molecules at a later stage, emit photons of specific wavelengths that are characteristic of the atomic species present on the surface of the canister and ablated into the plasma. This allows the detection of materials deposited on surfaces, even in relatively small concentrations. Both chlorine and iron (the major constituent of the steel canister) exhibit prominent atomic spectral lines in the infrared spectral region (Kramida et al., 2017). In particular, the Cl I spectral line at 837.6 nm is especially useful for the purpose of chlorine detection. By combining the methods of emission spectroscopy and carefully developing calibration curves (Gornushkin et al., 1999; David and Omenetto, 2010), a quantitative relationship can be established between the chlorine spectral line intensity and its corresponding concentration on a stainless steel surface. This approach has been explored by several research groups (Wilsch et al., 2005; Gehlen et al., 2009; Eto and Fujii, 2016), which have all encountered the challenge associated with the high ionization potential of chlorine. In order to address this challenge and to enhance the signal-to-background ratio for the spectral line observed, we used the double-pulse (DP) LIBS technique (Benedetti et al., 2005; Babushok et al., 2006). DP lasers are now commercially available and are becoming increasingly more compact (Li et al., 2017). In the DP technique, the first pulse ablates the target, while the second effectively reheats the plasma, mainly via the inverse bremsstrahlung mechanism,

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thus enhancing the signal. The DP method has already proven its success in the detection of chlorine on concrete surfaces (Labutin et al., 2013) and in an iron-oxide mixture (Pedarnig et al., 2014).

In the case of inspection of dry cask storage for used nuclear fuel, LIBS has to be compact and suitable for *in-situ* deployment. A multi-sensor robotic platform, dubbed the PRINSE (Proactive Robotic Inspection of Nuclear Storage Enclosures), has been developed to address a set of more comprehensive inspection requirements (Lissenden et al., 2016). The PRINSE system consists of a train that includes electromagnetic acoustic transducers, LIBS, and temperature and radiation sensors. This suite of sensors enable PRINSE to detect cracks, measure the concentrations of chlorine and other elements on the canister surface, and characterize the temperature and radiation field. Inside the payload area of the train car dedicated to LIBS, the optics is constrained to a height of 32 mm and a footprint of 100 mm × 80 mm. This spatial constraint poses a significant challenge in the engineering design of the LIBS delivery with commercial off-the-shelf optics. Additionally, since the robotic train is required to operate in a deep channel of a dry cask storage container that can only be accessed from its top, 25-m long optical fibers are used to deliver the laser pulse and collect and transport the light collected from the plasma radiation. In Fig. 1 we present the conceptual design and principle of operation of a fully portable, remotely delivered DP LIBS system capable of performing sensitive detection of trace elements on metal surfaces. We demonstrate its integration with the PRINSE multi-sensor robotic system and present the initial results of the determination of its detection limit for chlorine on stainless steel in a testbed that captures the relevant characteristics of dry cask storage systems.

2. Summary of feasibility study

Halogen elements can be challenging to detect via LIBS because their energy level distribution has many high-lying upper energy states. For example, the strongest resonance transitions of chlorine are in the vacuum ultraviolet spectral region, which is not suitable for LIBS measurements under typical ablation conditions due to absorption occurring in the atmosphere and in optical materials. However, the Cl I spectral line located at 837.6 nm is the most intense chlorine emission line outside the vacuum ultraviolet region, and has been shown to be readily detectable in LIBS. The limit of detection is typically in the tens of thousands of mg/l, but has been reduced significantly, by applying high incident laser energy (Wilsch et al., 2005; Gehlen et al., 2009; Tran et al., 2001; Burakov et al., 2007; Sugiyama et al., 2010), adopting helium buffer gas (Wilsch et al., 2005; Gehlen et al., 2009; Sugiyama et al., 2010), or using an additional excitation technique such as pulsed electric discharge (Burakov et al., 2007) and DP (Sugiyama et al., 2010; Labutin et al., 2014).

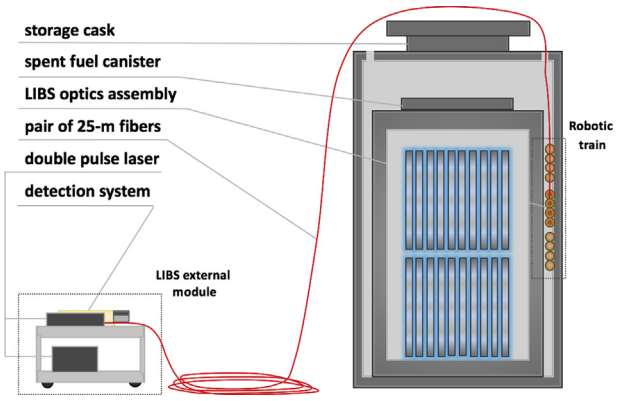

Fig. 1. Illustration of the design concept of a robotically delivered LIBS system for characterization of surface composition of the steel canister in dry cask storage.

The capability of LIBS to provide remote *in-situ* measurements of elemental concentrations is attractive for use in challenging environments such as dry cask storage containers. In addition to high temperature, another important aspect of the dry cask storage environment is the limited space and lack of direct line of sight of the inspected surface. These constraints can be overcome by fiber delivery of high-power laser pulses to the location of interest and the transport of collected optical emission from the plasma through the optical fiber. The bulky and temperature sensitive components of the LIBS system such as the laser, spectrometer, and fast-gated detector can be located outside the overpack. Additionally, optical fiber provides strong confinement of laser light, which shields the personnel from laser hazards and eliminates the possible effect of atmospheric turbulence on laser delivery and LIBS signal collection. The fiber probe can be carried by the robotic train, which eliminates the need for optical alignment along its path. Optical fibers show relatively high radiation tolerance in the near-infrared region (Saeki et al., 2014), and their composition can be further tailored to enhance radiation resistance (Girard et al., 2013; Nagasawa et al., 1984).

2.1. DP excitation in fiber-optic LIBS

The performance of fiber-optic LIBS is affected by several constraints that are not present in open-beam delivery, including the optical damage of the fiber that limits the peak power that can be delivered onto the sample surface, imperfect laser-fiber coupling that results in further reduction of peak power at the output of the fiber, intermodal dispersion that stretches the laser pulse after propagating through the fiber, and large beam divergence and limited focusability at the fiber output. These constraints limit the maximum achievable laser intensity necessary for observing chlorine emissions at low concentrations. In most prior successful “real world” applications of fiber-optic LIBS that require remote analysis to be made *in situ*, no special attention was paid to the halogen chlorine (Saeki et al., 2014; Davies et al., 1995; Cremers et al., 1995; Neuhauser et al., 2000; Rai et al., 2001; Whitehouse et al., 2001). The exception is the work of Eto and Fujii, who demonstrated the potential of detecting the Cl I emission (837.6 nm) at concentrations as low as 50 mg/m^2 using fiber-optic LIBS (Eto and Fujii, 2016). They used single-pulse excitation and a fiber length of 5 m. However, it remains desirable to further reduce the limit of detection and to conduct measurements over fiber distances exceeding 5 m.

In our recent work, the DP excitation technique was introduced in fiber-optic LIBS to improve its limit of detection for chlorine measurements (Xiao et al., 2018). By splitting a single laser pulse into two and delaying one of them to realize a DP configuration, more energy can be delivered through the optical fiber. In DP ablation a significant enhancement of the characteristic emission from plasma resulted due to a larger population of excited analyte atoms formed by reheating the preformed plasma. The enhanced material removal and increased atomized analyte atoms in the plasma volume also contribute to the enhancement of the characteristic emissions. An approximate 5-fold increase of the intensity of emission lines was achieved. This high emission intensity allowed the identification of the lines and quantification of the chlorine concentrations at levels as low as 5 mg/m^2 (Xiao et al., 2018). Furthermore, this increase of sensitivity was achieved concurrently with extending the fiber distance to 25 m, with possibility for future extension.

2.2. Laboratory testing overview

Initial laboratory tests were performed using a 10-ns, 10-Hz Nd:YAG laser (Quanta-Ray PRO-250-10, Spectra Physics). The fundamental wavelength of the Nd:YAG laser was used, since the signal-to-background ratio of the Cl I line induced by the 1064-nm laser pulse was experimentally determined to be much higher than that generated when using the second-harmonic (532 nm) wavelength. The energy of