

Harsh environment low cost LIBS sensor for sub-surface CO₂ leak detection in carbon sequestration

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ABSTRACT

Monitoring carbon sequestration poses numerous challenges to the sensor community. For example, the sub-surface environment is notoriously harsh, with large potential mechanical, thermal, and chemical stresses, making long-term stability and survival a challenge to any potential in situ monitoring method. Laser induced breakdown spectroscopy (LIBS) has been demonstrated as a promising technology for chemical monitoring of harsh environments and hard to reach places. LIBS has a real-time monitoring capability and can be used for the elemental and isotopic analysis of solid, liquid, and gas samples. The flexibility of the probe design and the use of fiber-optics has made LIBS particularly suited for remote measurements. The paper focuses on developing a LIBS instrument for downhole high-pressure, high-temperature brine experiments, where CO₂ leakage could result in changes in the trace mineral composition of an aquifer. The progress in fabricating a compact, robust, and simple LIBS sensor for widespread subsurface leak detection is presented.

Keywords: CO₂ sequestration, laser, LIBS sensor, downhole monitoring

1 INTRODUCTION

Geologic-carbon-sequestration (GCS) has the potential to store thousands of Gt of CO₂ in the United States alone [1]. In GCS, the CO₂ is prevented from entering the atmosphere, where it has been shown to be a major contributor to climate change. However, disposal of such large volumes in the sub-surface has potential to contaminate aquifers, so it will be important to verify that nearby underground sources of drinking water (USDW) is not contaminated [2]. Several conventional methods for monitoring have been proposed, including pressure and temperature monitoring, seismic monitoring, and sample extraction for off-site analysis [3].

Laser Induced Breakdown Spectroscopy (LIBS) has become a productive measurement technique with a wide range of methods and applications being vigorously pursued around the globe. LIBS uses one or more laser pulses to ablate and excite 1 – 1000 ng of sample mass into a plasma. The light from the plasma contains wavelengths that are characteristic of the atomic emission from elements inside the plasma. To generate the high energies needed for plasma creation, lasers in LIBS instrumentation often rely

on laser pulses that are shorter than a few tens of ns. In this fashion, a few mJ, or even tens of μ J energy, can create the high peak powers needed to overcome the dielectric breakdown of the material and produce the “spark” whereby the characteristic atomic emission light is generated.

Much of the recent growth in the field has come from the increasingly wide range of LIBS instruments developed in different laboratories and commercial entities [4]. In the commercial sector, these new instruments range from bench-top units that can be configured to operate in conjunction with laser ablation mass spectrometers to handheld devices configured for field use [5]. Similarly, there have been several custom-designed instruments that have taken LIBS into harsh environments (i.e., Mars, ocean deep thermal vent), where typical approaches would be impossible [6,7]. This paper describes development of a field-deployable LIBS instrument for downhole measurement of CO₂ leaks in carbon sequestration. LIBS has the potential for deployment inside a well, monitoring the cationic composition of the aquifer at the temperature and pressure at depth and removing the potential confounders introduced by sample extraction

2 LIBS MEASUREMENTS IN DOWNHOLE ENVIRONMENT

Downhole environments can be highly saline and pressurized to tens to hundreds of atmospheres. These two variables constitute very strong matrix effects, causing variation in the pressure or salinity to change the LIBS spark characteristics of a given trace element. To evaluate the direct effect of elevated CO₂ on the LIBS signal, the plasma was formed in the presence of a pure carbon dioxide atmosphere at the given gas pressures (i.e., 10, 50, and 120 bar). The effect of pressure and water solubility on the LIBS signal was studied in an aqueous solution of 1000 mg·L⁻¹ calcium chloride (CaCl₂·2H₂O), offering a high signal-to-background ratio for the Ca I 422.67 nm emission line. The solution was prepared by dissolving CaCl₂ salt in ultrapure water.

Figure 1 shows that the 422.67 nm Ca emission line intensity is dramatically reduced under high pressure CO₂ [8]. A CO₂ pressure of 10 bar produces a 37% reduction and at 120 bar, the emission intensity drops by 70%. These results are indicative of the direct effect of the gas pressure on Ca emission intensity. As is characteristic of the rapid cooling of plasma underwater, the Ca emission lines exhibit a short lifetime under different atmospheres and pressure

conditions. The calcium neutral line exhibited emission lifetime in the range of 120 - 300 ns. A large difference between the intensity of the Ca lines obtained in ambient pressure and in the presence of CO₂ is observed for gate delays less than 100 ns. As the delay increases, the intensities decrease continuously with almost constant exponential decay as a function of pressure [9].

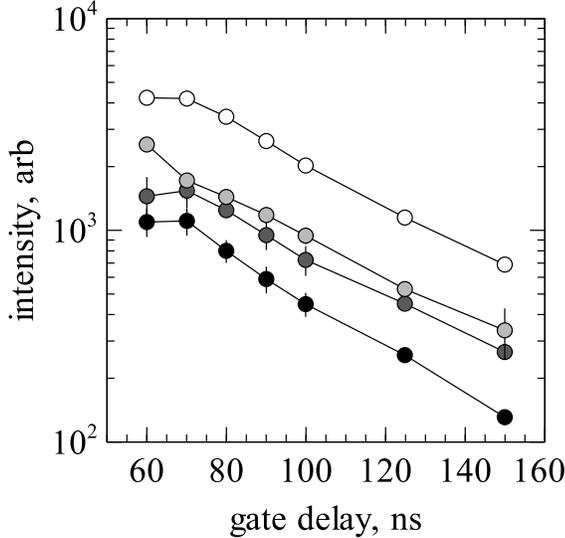


Figure 1: Signal intensity of Ca I 422.67 nm emission lines as a function of gate delay for both ambient pressure (open circles) and at 10, 50, and 120 bar (light gray, dark gray, and filled circles, respectively) [10].

Likewise, the effects of high salinity on the LIBS emission spectra have received limited attention. For instance, Cremers et al. [11] reported that the intensity ratio between the Ca II 393.37 nm and Ca I 422.67 nm lines decreases with the addition of sodium chloride (NaCl) to a 100 mg L⁻¹ Ca-water solution. Michel et al. [12] observed that the addition of 254 and 25 400 mg·L⁻¹ NaCl to a solution of 1000 mg·L⁻¹ Ca (at 2.57×10⁷ Pa) produced an increase in the emission intensity of the Ca I 422.67 nm line, while no significant increase was observed for the Ca II lines at 393.37 nm and 396.85 nm. Thornton et al [7] compared the spectra of Li and Ca obtained with and without 11,035 mg·L⁻¹ Na. They observed that Na enhances the signal intensity of the Li (670 nm) and Ca (422.67 nm) lines. These studies are illustrative of the NaCl matrix effect on the LIBS signal of Ca.

Although the effect of cation-based matrix effect was studied, the effect of anion based matrix effect has received less attention. This is relevant to CO₂ storage because the chemical composition of groundwater is influenced by the minerals and gases reacting with the water in its relatively slow passage through the rocks and sediments of the earth's crust. The geological formations at and around a storage site may include a wide range of minerals and the composition of these minerals may be affected when aqueous chemical equilibria are modified by the leaking CO₂. Water that circulates in limestone may contain

bicarbonates/carbonates alkalinity. Chloride and sulfate are also present in groundwater. Because neither chloride nor sulfate takes part in typical biological or chemical reactions, they tend to concentrate in shallow groundwater over time.

To examine the matrix effect of sodium salts of chloride, sulfate, and carbonate on the LIBS measurement of Li and K, we prepared solutions by mixing LiCl and KCl salts with NaCl, Na₂CO₃, and Na₂SO₄ [13]. Three sets of samples containing 10³, 10⁴, and 10⁵ ppm of NaCl, Na₂CO₃, and Na₂SO₄ were prepared. By dividing the resulting LIBS signal by the expectation value from the calibration curve for that concentration, a normalized matrix effect can be estimated. This normalized matrix effect for Li⁺ and K⁺ is plotted in Figure 2 for the three mentioned salts. As evidence of matrix effect, a clear dependence of sample matrix can be seen on the Li I and K I emission line intensities. For NaCl, an increase in the intensity of the emission lines is observed with the addition of 0.1 – 1% NaCl. For Na₂CO₃, there is a reduction in the emission line intensities across all concentrations. However, for Na₂SO₄, there is a little change compared to the control solution, even at 10% salt concentration. Generally the normalized matrix effect shows a slight decrease in the signal as a function of trace metal concentration.

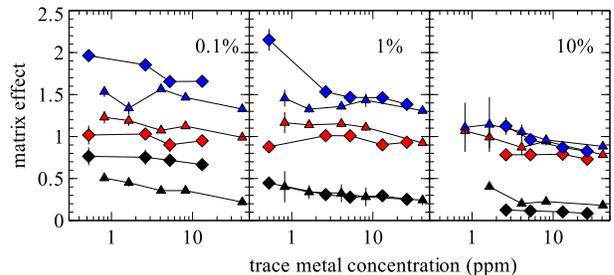


Figure 2: The effect of 0.1, 1, and 10% solutions of NaCl (blue), Na₂SO₄ (red), and Na₂CO₃ (black) on the calibration curves of Li⁺ (▲) and K⁺ (◆) is shown. The y-axis displays the measured intensity divided by the value given by the calibration curve for that concentration [10].

A comparison of matrix effects indicate that in the presence of dissolved sodium compounds the emission line intensities vary in the following order: NaCl > Na₂SO₄ > Na₂CO₃. For instance, when compared to the pure solution, the intensity of Li emission line obtained in LiCl + 1000 ppm NaCl and LiCl + 1000 ppm Na₂SO₄ samples ([Li⁺] = 1.6 ppm) increases by 2- and 1.5-fold, whereas the line intensity decreases by half using LiCl + 1000 ppm Na₂CO₃ sample. This behavior seems to be related to the difference of thermal properties between aqueous NaCl, Na₂SO₄ and Na₂CO₃, such as boiling point (NaCl, 1690 K; Na₂SO₄, 1700 K; Na₂CO₃, 1870 K) and thermal conductivity (NaCl, 6.5 W·m⁻¹ K⁻¹; Na₂SO₄, 1.0 W·m⁻¹ K⁻¹; Na₂CO₃, 0.6 W·m⁻¹ K⁻¹ at 300 K). Figure 2 also shows that underwater LIBS signal is detectable in high salinity water (i.e. for a sodium salt concentration up to 10⁵ ppm), thereby

demonstrating the feasibility of using LIBS for saline groundwater monitoring.

3 INSTRUMENT CONSIDERATION

To meet the demands of downhole environments, the traditional LIBS configuration will require modification in several areas. All the expensive and sensitive equipment needs to be placed at the surface avoiding the downhole dangerous environment. Unfortunately, the peak laser pulse energies required to generate LIBS sparks in aqueous environments are much higher than the thresholds of conventional optical fibers. If the beam path can be fiber coupled by separating the measurement head from the spectrometer, we are can keep the more expensive equipment at the surface, reducing the engineering burden and cost of deployment. The measurement head must be fabricated to be (1) small, (2) robust and (3) low cost. This allows the least expensive components to be placed in the most dangerous environment, minimizing the engineering burden and cost of deployment.

Another important consideration is the type and configuration of pulsed laser to be used. Many laboratory studies carried out on aqueous LIBS have demonstrated the benefits of the double-pulse LIBS (DP-LIBS) [14]. In this configuration, the first laser pulse is used to initiate the formation of a bubble or cavity. LIBS light is collected from the second pulse. This produces a higher quality signal than the conventional single-pulse LIBS. As desirable as this may be, there is substantial cost and complexity to using a DP-LIBS approach for downhole applications, most of which hinge around the difficulty of timing the second pulse. To properly and precisely trigger the second laser pulse at the appointed time, an active Q-switch laser would be necessary, which would add substantial difficulty to the measurement. Accommodating the equipment necessary for active Q-switch lasers—Pockels cell, waveplate, output coupler, high reflector, polarizer, gain medium, and pump source—in the well bore is possible, but not without substantial cost and complexity. Furthermore, as useful as this may be, we have demonstrated successful use of single-pulse LIBS in synthetic brines at temperature.

Instead of the common active Q-switch laser, we have proposed the use of a passive Q-switch laser that is fiber coupled to an end-pump and spectrometer, as depicted in Figure 3 [10]. The passive Q-switch allows the laser to be driven only by a pump laser at the surface that is fiber-coupled to the end-pumped laser rod downhole. Once the laser fires and a spark is generated, the light from the spark can be directed around the laser rod and back into the optical fiber. By using a pulse detector, the LIBS spectrometer can be triggered to capture the spectrum at a specific gate delay. Once the spectrum is recorded, it can be transmitted in digital format over to a computer that handles the power, data storage, processing, and control of the instrument. This allows all of the electronic circuitry to

remain at the surface, where the risks (and detector array temperature) can be more easily controlled, while allowing the LIBS measurement to be taken at depth.

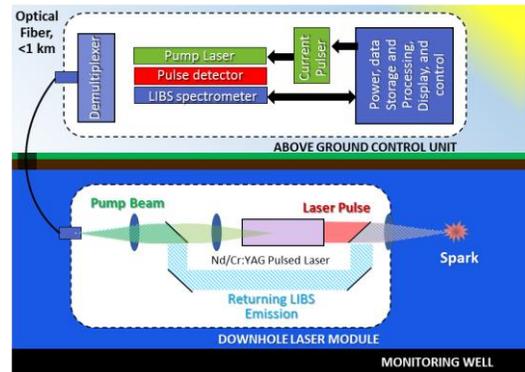


Figure 3: A schematic for operation of a downhole LIBS monitoring system with a control unit above ground. The control unit has the pump laser, spectrometer, and timing circuitry to operate the pulsed laser and measure the LIBS signal. The downhole laser module is equipped with a separate beam path that allows the LIBS light to be coupled back into the optical fiber connected to the control unit.

Our first prototype is shown below in Figure 4. It consists of a passive Q-switch laser rod that is affixed inside of a housing. The housing is constructed from components purchase from Thorlabs and modified with light machining and customization. The housing contains a fiber coupler, pump laser focusing lens, and pulsed laser focusing lens. The entire assembly is only 6.2 cm in length, 1.3 cm in width, and 32 g in weight. At economies of scale, the device cost would be a small fraction of the rest of the equipment necessary to carry out a LIBS measurement. This initial design can be modified to accommodate the requirements of a downhole LIBS system, but it is also suitable for other applications with tight mass and volume requirements.



Figure 4: On the top, a model of the passive Q-switch laser and, on the bottom, the finished prototype [10]

4 CONCLUSIONS

The work presented here outlines how LIBS can be adapted to the unique challenges of downhole environments. As the technologies develop, LIBS may acquire the ability to deploy additional capabilities beyond elemental concentration monitoring in harsh environments, such as Raman spectroscopy [15] and Laser Ablation Molecular Isotopic Mass Spectrometry (LAMIS) [16], which would allow a wider range of measurements to be carried out by a robust, remote LIBS probe. Distribution of many laser spark sources would add the capability to monitor a wide area across CO₂ storage sites [17]. The continued development of LIBS for these applications has the potential to migrate LIBS from the laboratory to the field site and crucial measurements and services along the way.

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