LIBS characterization of algal fouling on insulators

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Abstract
Algae contamination accumulated on the surface of insulators will affect the electrical properties of insulators. At present, the characterization method of algae contamination is the image method, which determines the distribution of algae contamination through colour. The detection results are affected by environmental changes and the growth state of algae. This paper puts forward a method of detecting polluted insulator surface with algae by using laser-induced breakdown spectroscopy (LIBS) technique, combined with the scanning electron microscope (SEM), inductively coupled plasma emission spectrometer (ICP), analyzed by the spectra of algae contamination. Mg, Ca, Fe are selected as the analytical element. The classification of algae contamination, non-algae contamination and no contamination are realized with the principal component analysis (PCA). The research results are of great significance for characterization of algal pollution on insulator surface by LIBS.

1 | INTRODUCTION

In recent years, in Sichuan, Guangxi, Yunnan, and other regions in China, algae have been found to grow on the surface of room temperature vulcanization (RTV) coatings of insulators to varying degrees. Studies have shown that, in hot and humid environments, the insulator surface is prone to algal growth and accumulation of algal fouling. Differences in the growth status, distribution, and stacking thickness of algae will affect the electrical properties of insulators such as the hydrophobicity and flashover voltage [1–3]. Previously, our research team studied the image detection method of algae on insulator surfaces and developed an image-based detection method of the algae number on the surface of silicone rubber under different light and shooting angles [4]. The parameters (algae coverage and characteristic green value) that characterize the algae coverage area ratio and the growth thickness per unit area were studied. The image method can be used to characterize the algae coverage on the insulator surface. However, fouling on the surface of the insulator is complicated, and there may be some errors in judging the fouling components only by the fouling colour.

Algae is able to absorb heavy metal components in water bodies and plays an important role in environmental ecological restoration and regulation. As a detection method, laser-induced breakdown spectroscopy (LIBS) is used by researchers to analyze algae in water bodies and determine the elemental composition and compound composition of algae cells, and this information can be used as an indicator of water pollution to confirm the existence of heavy metal elements.

Porizka et al. [5] in the Czech Republic performed LIBS detection of Chlamydomonas reinhardtii and Trachydiscus minutus in water. There are three different methods of pre-treatment for the experiment: an algae jet, an algal biofilm, and an algal suspension. Corresponding to the pre-processing method of the experiment, there are some differences in the settings of the laser pulses, which include a collinear double-pulse laser, a double-pulse trigger, and an orthogonal double-pulse. By analyzing the spectral data obtained by the three methods, it can be determined that the metal elements K, Ca, Na, and Mg are present in the algae.

Garcimuno et al. [6] of Argentina used calcium hydroxide powder as a binder to suppress algae into solids and performed
LIBS analysis. The atomic spectral lines of copper and other trace elements were detected. Quantitative analysis of copper showed that the detection limit of copper in this algae sample reached 9 ppm.

At present, the application of LIBS in algae testing is mainly for algae in water bodies, and the main purpose is to reflect the pollution of water bodies. These experiments generally do not involve LIBS analysis of algae that has survived in a solid environment. As a supplement to the image method, this paper uses LIBS to study the composition of the characteristic elements in algal fouling. Furthermore, a qualitative analysis and a quantitative detection of the characteristic elements in algal fouling on insulators are conducted to explore the feasibility of LIBS for characterizing algal fouling.

2 EXPERIMENT

2.1 Experimental device

As shown in Figure 1, the LIBS system is mainly composed of four parts: a laser, an optical path system, a controller, and a spectrometer. The experimental LIBS device belongs to the Laboratory of Electrical Engineering and Energy, Graduate School at Shenzhen, Tsinghua University. The nanosecond pulse laser is a Nimma-900 model, the wavelength can be set to 1064, 532, and 266 nm, the pulse width is 8 ns, and the laser energy can be adjusted up to 110 mJ. The optical fibre spectrometer is an Avantes-Rackmount model, the spectral range is 200–640 nm, and the resolution is 0.09–0.13 nm. The digital delay generator is an SRS-DG645 model with eight channels, 200–640 nm, and the resolution is 0.09–0.13 nm. The digital delay generator sends out a signal again to control the optical accessory, and a plasma is generated instantaneously; the digital delay generator sends a signal to adjust the laser energy; the elemental energy is excited to excite the spectrum under high energy; and the emission spectrum is measured under the LIBS device. The ICP instrument used is an Arcos II MV type test instrument made by SPECTRO Analytical Instruments Inc. in Germany.

A scanning electron microscope (SEM) was used to observe the ablation morphology of the sample surface after two bombardments under experimental conditions. A ZEISS SUPRA 55 model SEM was employed. Metal spray coating using a Leica EMACE 200 model was used to increase the surface conductivity of the test sample. Pt gold spray material was utilized.

ICP is mainly used in the qualitative and quantitative analysis of multiple inorganic elements. Its advantages are the simultaneous detection of multiple elements, low detection limits, high measurement accuracy, and repeatability. Its disadvantages are the complexity of sample pretreatment and the relatively high level of operation. As a high-precision chemical analysis method, ICP is widely used in elemental analysis in materials, medicine, and biology. The work content of ICP detection is mainly divided into three parts: the liquid sample is introduced into the ICP light source cavity after being evaporated under the laser energy; the elemental energy is excited to excite the spectrum under high energy; and the emission spectrum is analyzed by a spectrometer for quantitative determination of ions or atoms. When performing ICP experiments on insulator samples, because ICP injection requires a liquid, a digester (hydrofluoric acid) is required to pre-process the sample.

According to the relevant literature, algal organisms usually contain calcium, magnesium, iron, zinc, manganese, and copper, and the concentration of these elements is determined by ICP.

FIGURE 1 Schematic diagram of the LIBS device

The parameters of the instrument were selected as follows: the unit laser energy density was 305.57 mJ/mm², the light receiving angle was 75°, and the spectrometer delay time was 1 µs.

2.2 Sample and experimental parameters

This experimental sample is algal fouling grown naturally on the RTV coating of the retired insulator. The laser pulse is incident perpendicular to the sample, and the spot diameter on the sample after focusing is approximately 0.5 mm.

According to the growth pattern and characteristics of algae, they mainly contain chlorophyll, and the elements that make up chlorophyll are C, H, O, Mg, and N. Ca and Fe in algae are involved in synthesizing various enzymes required by the metabolism; other natural pollution mainly contains Ca, Na, and Mg; and the main elements that make up RTV silicone rubber are Si, O, C, Al, and Fe. The measurement of H and O is susceptible to the influence of environmental humidity, and the measurement of N is susceptible to the influence of nitrogen in the air; therefore, C, Mg, Ca, and Fe are selected as the main elements to be analyzed.

An inductively coupled plasma emission spectrometer (ICP) was used to measure the concentration of elements in insulator samples with and without algal fouling and compared with the spectral data measured by LIBS experiments to determine the characteristic elements that can be used for algal fouling analysis. The ICP instrument used is an Arcos II MV type test instrument made by SPECTRO Analytical Instruments Inc. in Germany.

According to the relevant literature, algal organisms usually contain calcium, magnesium, iron, zinc, manganese, and copper, and the concentration of these elements is determined by ICP.
RESULTS AND DISCUSSION

3.1 Topography of LIBS ablation insulator surface

Since the fouling is distributed in the form of a thin layer on the surface of the insulator, when a laser pulse is applied to the sample, the plasma easily penetrates the thin layer directly to the surface of the insulator substrate, causing the spectrum to contain both fouling information and matrix information, which not only affects the accuracy of fouling analysis but may also damage the insulator substrate and affect its electrical performance.

The SEM was used to observe the ablation morphology of the sample surface after two bombardments under experimental conditions (laser energy 60 mJ), as shown in Figure 2 and Figure 3. It can be seen that when the laser is applied to the surface of the sample for the first time, only the fouling layer is ablated; when the laser is applied to the surface of the sample for the second time, the laser ablated holes become larger, and obvious traces are formed after laser ablation of the insulator substrate during the second bombardment. Thus, to obtain information about the algal fouling without damaging the insulator substrate, only one bombardment is required.

3.2 Intensity of the spectral line of the elements under repeated pulses

Five points on the surface of the algae-covered silicone rubber were selected, and LIBS laser pulse experiments were repeated on the algae-coated insulators and an average of the spectrum data was calculated. The relationship between the spectral line intensity and the ablation depth was analyzed. The experimental results of five LIBS bombardments on the algae-coated insulator are shown in Figure 4. To clarify the relationship between the intensity of the spectral line and the change in ablation depth, it is necessary to select the element with a relatively higher spectral intensity in the emission spectrum for analysis. With reference to the related research on algae LIBS, Mg, Ca, Al, Na, and Fe were selected as the objects of laser ablation.

The intensity of the characteristic spectral line of Mg decreases as the number of bombardments (ablation depth) increases; the intensity of the spectral lines of Ca and Na reaches the maximum during the first bombardment, and the intensity of the spectral line decreases rapidly during the second bombardment and slightly increases thereafter. The intensity of the Al line does not change much, and the intensity of the Fe line increases as the number of bombardments increases.

The main components of silicone rubber insulators are white carbon black (silicon dioxide), aluminum oxide, vulcanizing silicone rubber, ferric oxide, and other fillers; the raw materials contain only a small amount of Na and Mg compounds; the main components of natural fouling are usually NaCl, MgCl₂, and CaSO₄.

As the number of LIBS pulses increases, the craters formed by laser ablation become deeper, and the ablation range is expanded to the surroundings. The edge of the crater will
inhibit the expansion of the plasma; the crater will deepen after repeated pulses; and the position of the laser and the sample will be outside the focal length of the lens, which will reduce the energy density of the laser on the surface of the sample.

A variety of factors work together to cause a certain change in the intensity of the spectral line of the elements under repeated pulses. For elements that exist only in natural fouling, the spectral line strength reaches its maximum value during the first bombardment; for elements that exist in the matrix of the silicone rubber insulator, the spectral line strength gradually increases as the number of bombardments increases.

### 3.3 Analysis of the characteristic elements of algal fouling cover

As shown in Figure 5, the experimental samples are marked from left to right as #1–#4, where #1–#3 are RTV samples taken at different locations of the Sichuan algae insulator, and #4 is a sample from the Sichuan algae insulator after non-contaminated RTV samples were obtained after treatment with deionized water and absolute ethanol. Each piece is approximately 5 cm × 5 cm in size.

The reason for the high concentration of aluminum and iron is that, in the ICP experiment, the algal fouling was treated, and the RTV coating was directly treated as a sample. The RTV coating itself contains a large amount of iron and aluminum. Compared with the ICP test results of #1–#3 and #4 as shown in Table 1, it can be confirmed that there are mainly three metal elements in the algal fouling: magnesium, calcium, and zinc as shown in Figure 4. Since the concentrations of iron and aluminum in the RTV sample are too large, it is impossible to determine if the algal fouling contains iron or aluminum based on the results of ICP; furthermore, the intensity of the characteristic spectral lines of other elements may be affected, causing deviations in the detection of the element concentrations.

Samples #1–#4 are bombarded with LIBS. Ten points are selected in the middle and four corners of the sample, and each point is bombarded once, and the ten spectral data are averaged as the spectral line intensities that characterize the sample. When the LIBS spectrum obtained under the same conditions is superimposed, as shown in Figure 6, it can be seen that the components in the fouling are complex, and there are many types of elements which make the spectral line strength of the algae-coated silicone rubber and the non-algae-coated silicone rubber differ greatly. Among them, Mg, Ca, and Na are much more abundant in the algae-coated part than in the non-algae-coated part, and Si and Al are much more abundant in the non-algae-coated part than in the algae-coated part. According to the study described in the previous section, when LIBS bombards the fouling layer only once, there is almost no damage done to the silicone rubber, and the spectral intensity of Fe in the algal-covered silicone rubber sample is still relatively high. It can be considered that Fe is also present in the algal fouling. In summary, the full spectrum confirmed that the characteristic elements in algal fouling were mainly Mg, Ca, Fe, and Na.

The properties of each element emitted by the plasma are different, and the information acquisition of each element is easily affected by the LIBS experimental device and parameters. Therefore, LIBS cannot effectively detect all elements in the algal fouling. Compared with the conclusions obtained by ICP,
the detection results of LIBS cannot determine the presence of Mn, Cu, and Zn in algal fouling.

3.4 Principal component analysis model to distinguish fouling types

Simple analysis of the intensity of the spectral line of a single element in the LIBS experiment cannot distinguish between algal fouling and non-algal fouling intuitively and quickly. As an important method of spectral chemometric analysis, principal component analysis (PCA) can achieve cluster analysis of variables and determine algal fouling, non-algal fouling, and non-fouling.

PCA is a data dimensionality reduction algorithm. Its basic principle is to project the related variables in a matrix into another set of uncorrelated vectors through linear transformation to extract the main feature components of the data [7].

LIBS was used to analyze three types of silicone rubber insulators without fouling, with natural fouling without algae, and with algal fouling. For the above three types of insulators containing different types of fouling, six different positions were taken for testing. According to the ablation of the sample, under the optimized experimental parameters, the fouling layer had been penetrated during the first bombardment of LIBS. When analyzing the fouling components, to avoid damaging the insulator substrate, only one bombardment was performed, and the spectral data obtained from the first ablation were analyzed.

The data obtained through LIBS were used as the input matrix after normalizing the spectral lines of the experiment; the Unscrambler X software was used to complete the analysis and output the PCA model.

As shown in Figure 7, the cumulative contribution rate graph shows that the contribution rate of the first two factors (PC-1, PC-2) when interpreting the input data reached 96%. Plotting the distribution of scores under two factors of different samples, as shown in Figure 8, we can see that the six different types of fouling, C1, C2, C3, C4, C5 and C6 (excluding fouling), N1, N2, N3, N4, N5 and N6 (including natural fouling), and Z1, Z2, Z3, Z4, Z5 and Z6 (including algal fouling) can be distinguished by the PCA model. N1, N2, N3, N4, N5 and N6 and Z1, Z2, Z3, Z4, Z5 and Z6 are slightly separated while clustering, while C2, C3, C4 are almost clustered at one point. This finding indicates that the LIBS signals of the insulators without fouling show a strong similarity, and the LIBS signals of the insulators with algae or natural fouling are slightly different.

4 CONCLUSIONS

With the help of SEM and ICP, the ablation characteristics of algal fouling were studied through LIBS experiments. The feasibility of LIBS for qualitative analysis and quantitative detection of algal fouling was explored. The following three conclusions were obtained:

1. When the laser energy is 60 mJ, a single bombardment of the surface of the algae-coated insulator by LIBS will not damage the insulator substrate.
2. The high accuracy and good stability of the ICP method for the detection of insulators with algal fouling shows that the content of Al and Fe is too high; with the exception of Na, Ca, and Zn, the content of other metal elements is very low. The characteristic elements that can be used for LIBS detection in algal fouling are mainly Mg, Ca, and Fe.
3. PCA can be used to classify three different situations: algal fouling, non-algae natural fouling, and non-fouling.

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