

# ***IN-SITU* MONITORING OF ADDITIONS TO LIQUID SLAG USING LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)**

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## **Introduction**

Laser-induced breakdown spectroscopy (LIBS) is an analytical technique which uses a pulsed laser to initiate plasma formation at the surface of materials. The resulting plasma is characteristic for the material's elemental composition.<sup>1</sup> A pulsed laser is focused on the sample, which starts to heat up locally. The material evaporates and eventually a plasma is formed at the surface. The light of the plasma is collected using lenses and fibre optic cables, which transport the signal to a spectrometer. The resolved spectrum can subsequently be used to determine the present elements. Due to its rather simple setup, the LIBS technique is versatile and can be tailored to the application. Hence, it is attractive for rapid *in-situ* measurements of slag and metal in running furnaces.<sup>2-4</sup>

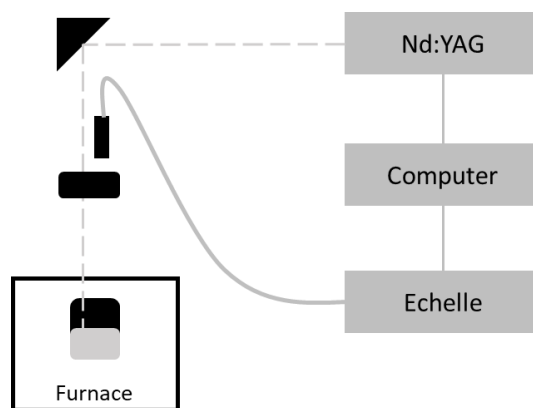
*In-situ* monitoring of the chemical composition of the slag will result in a stronger control over the melt and an improved end product quality. A higher process efficiency can be achieved and there is an economic and ecological benefit.

The *in-situ* monitoring of Cr, Cu, Mn and Ni additions have been reported in liquid steel,<sup>4</sup> however, the influence of additions to a fayalitic slag is unknown. Therefore, the additions of CuO and ZnO to a synthetic FeO<sub>x</sub>-SiO<sub>2</sub> rich slag at high temperature are monitored during the present study, as a first step to evaluate the suitability of LIBS for the on-line quantification of minor elements in the slag.

## **Materials and methods**

The sample was placed in a Ni-crucible in a furnace and heated up to a temperature of 1300°C in an Ar atmosphere in the laboratories of Energy Research Company (ERCo) in Plainfield, NJ. A Nd:YAG laser was used at its fundamental wavelength of 1064 nm to induce a plasma at the surface of the sample. A laser energy of 330 mJ, a pulse duration 6 ns and a frequency of 1 Hz were applied. The laser pulse was focused

on the surface using a concave lens. The light of the induced plasma was collected through the same lens and focused on a fibre optic cable, which was linked to an Echelle type spectrometer, resolving a spectral range of 200 nm to 780 nm. The broad spectral range allows the simultaneous detection of all elements of interest. Figure 1 shows a schematic overview of the LIBS system.



**Figure 1:** Schematic overview of the LIBS setup used in this study

The LIBS measurements were performed on a starting slag with a  $\text{FeO}_x\text{-SiO}_2$  rich matrix at a temperature of  $1300^\circ\text{C}$ . Table 1 lists the composition of the starting slag and the added CuO and ZnO compounds. CaO is added to promote a more liquid slag. This slag type mimics the fayalitic slag system. The measurements start at zero concentration and analytical grade CuO and ZnO powders were added in steps to the melt and measured using LIBS.

**Table 1:** Compositional range of the melt with a starting slag of 510 g (g)

	Starting slag	CuO addition	ZnO addition	
$\text{FeO}_x$	279.7	279.7	279.7	
$\text{SiO}_2$	186.5	186.5	186.5	
CaO	43.9	43.9	43.9	
CuO	-	+ 4 x 1.3	5.3	
ZnO	-	-	+ 9.0	+ 8.6
			+ 7.8	+ 5.0

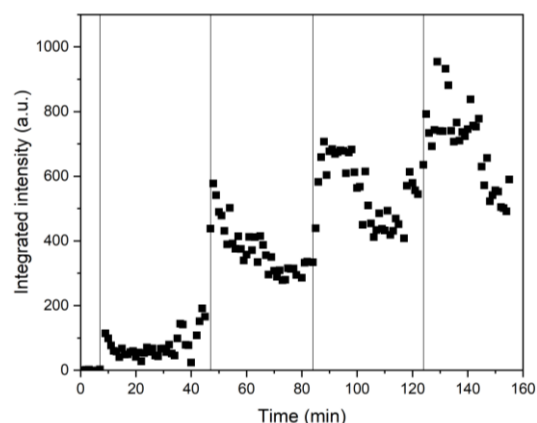
As a first addition, a weighted amount of CuO powder was added to the melt and mixed using a steel bar. Every minute a total of 25 spectra were collected of the melt surface and averaged in order to monitor the Cu content. After more than half an hour, the same amount of CuO powder was mixed in the melt. This was repeated until a total of four additions, with a total weight of 5.3 g in 510 g starting slag. Similarly, a known amount of ZnO powder was added to the melt and the Zn signal was measured. The first addition of ZnO powder weighted 9.0 g, during the next steps

the amount of ZnO addition was decreased step by step to a weight of 5.0 g, since the melt was getting more viscous with each ZnO addition.

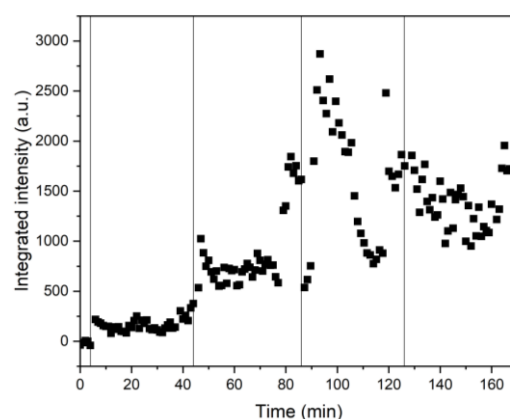
After collecting the LIBS spectra of the melt, an emission line was chosen for each element and the area below the line was calculated and used to plot the graphs. The lines were carefully selected; lines with strong signals were considered and lines which showed interference with other lines were avoided. The following atomic lines were selected: Cu 510.5 nm and Zn 481.1 nm.

## Results and discussion

Overall, the intensity increases with the addition of CuO and ZnO to the melt, as can be expected (Figures 2 and 3, respectively). It can be observed that there is a significant increase in Cu 510.5 nm signal with every addition of CuO to the melt. After the initial peak, the signal decreases. Note that the LIBS signals are collected from the surface of the melt, the same location where the CuO powder is added to the sample. The higher concentration of CuO powder on the surface of the melt results in higher intensities. Over time, the CuO dissolves in the melt and the overall Cu signal drops.



**Figure 2:** Signal increase of Cu 510.5 nm with the addition of CuO; The vertical lines indicate an addition of CuO to the molten slag



**Figure 3:** Signal increase of Zn 481.1 nm with the addition of ZnO; The vertical lines indicate an addition of ZnO to the molten slag

A similar trend can be observed for the Zn 481.1 nm line during the first two hours. Afterwards, starting from the third addition and continuing to the end of the measurements, the Zn signal appears to be more scattered. This is due to the increase in viscosity of the melt. Note that a higher volume of relatively cold ZnO powder is added to the melt in comparison to the volume of the added CuO powder, resulting in a temporary decrease in temperature and an introduction of more oxygen to the melt, promoting the formation of stable phases. These physical factors contribute to

the increase in viscosity of the melt, preventing a good mixing of the slag. Therefore, a more heterogeneous sample is obtained, which causes large variations in the Zn signal throughout the measurements.

The addition of Cr, Cu, Mn and Ni were successfully monitored in liquid steel in previous research by Gruber *et al.*<sup>4</sup> They recorded the addition of Cr to concentrations of 13.8 wt%, Cu to 0.54 wt%, Mn to 2.5 wt% and Ni to 5.92 wt%. In contrast to this study, a stable increase was observed with every addition. The more scattered data in the present study is caused by the viscosity of the melt, which introduces a heterogeneous aspect to the sample.

## Conclusion

In the present study, it has been shown that the LIBS technique can monitor the addition of CuO and ZnO to the slag until the melt surpasses a certain viscosity threshold, which limits the mixing of the additions in the melt and results in a heterogeneous sample.

With an appropriate addition methodology, a complete quantification can be made when standard samples are used with known composition. These samples can then be used to build calibration models to quantify unknown samples.

## Acknowledgement

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## References

1. F. Brech, L. Cross, "Optical microemission stimulated by a ruby maser", *Appl Spectrosc*, **16** 59 (1962).
2. E.F. Runge, R.W. Minck, F.R. Bryan, "Spectrochemical analysis using a pulsed laser source", in *Spectrochim Acta*, **20** (4) 733-736 (1963).
3. V. Sturm, R. Fleige, M. de Kanter, R. Leitner, K. Pilz, D. Fischer, G. Hubmer and R. Noll, "Laser-induced breakdown spectroscopy for 24/7 automatic liquid slag analysis at a steel works", *Anal Chem*, **86** 9687-92 (2014).
4. J. Gruber, J. Heitz, H. Strasser, D. Bäuerle and N. Ramaseder, "Rapid in-situ analysis of liquid steel by laser-induced breakdown spectroscopy", *Spectrochim Acta Part B*, **56** 685-693 (2001).