

Portable Elemental Analysis Device for Real-Time Chemical Analysis of Aluminium

Rauan Meirbekova¹, Sveinn Gudmundsson² and Kristjan Leosson³

1. Chief Metallurgist

2. Chief Technology Officer

3. Chief Scientific Officer

DTE, Arleynir 8, 112 Reykjavik

Corresponding author: rauan@dte.ai

Abstract



The operation of aluminium reduction cells relies on frequent sampling and chemical analysis. The sampling and analysis process is time-consuming and carries the risk of introducing measurement errors related to sample preparation and handling. This paper presents a portable device that uses Liquid Phase Laser-Induced Breakdown Spectroscopy (LP-LIBS) to analyze liquid metal composition down to below 10 ppm in a matter of seconds. In routine operation, the full cycle time for obtaining the chemical composition from a series of cells is below 90 seconds per cell. The correlations of analysis results with the conventional analysis method, spark optical emission spectroscopy (spark-OES), are also discussed. In addition to improving process control, monitoring the aluminium chemistry next to the cells also provides immediate results upon which operator can react to risk situations such as cathode failure/tap-outs. The potential offered by using machine learning and chemical analysis data to predict such failures is described.

Keywords: LIBS, Chemical analysis, Aluminium.

1. Introduction

The capital and operational costs of aluminium production are escalating, and cathode life contributes to one of the significant costs, where a cathode may cost more than \$150 000 in materials and human resources [1]. The word cathode is used in the aluminium industry to describe the entire contents of the steel shell that contains the molten metal and the electrolyte. This includes the electrically conducting carbon lining with current collector bars, refractories, and insulation material. There are different contributing factors to the cathode life, but according to [2], the cathode itself contributes 50 %, while the other 50 % comes from operational procedures. Thus, improving the process by frequently monitoring the aluminium chemistry and avoiding cell leaks/tap-outs can significantly save cathode costs. Tap-outs usually start due to cracks or holes in the cathode lining that gradually reach out to the collector bars. If the cracks open, the molten aluminium begins to penetrate and fill the gap, which may initiate the cathode failure of the lining. The cathode failure can be a bottom failure (high Fe, high Cu tap-out through collector bars) or side failure (high Si, red side, side tap-out, SiC lining). Both types of failures are equally important [3]. The contamination of liquid aluminium by Fe, Si or Cu can give valuable information on materials problems, operational problems, bath ratio control, and cell heat balance. It can be particularly important when old cells are pushed to their limits with the line current. All plants record tap-outs and their causes, the most common being cell age. Cathode failures can also be accompanied by increased cathode voltage, overheated shell, cathode lining temperature, and contaminated aluminium. Such recorded data may be useful to track the operational parameters and materials and they are important to predict the future behavior of cells. Early prediction can help assist cell maintenance, such as plugging the hole or gap by flake alumina. The plugging of aluminium-infiltrated cracks is crucial. This helps avoid further damage and limit the extension of the cracks, which can be intensified by electromagnetic turbulence and chemical erosion.

The company DTE has been developing stationary and portable elemental analyzers for liquid aluminium, along with a machine-learning-based cloud platform (IREAS) that helps to maximize plant efficiencies, sustainability and cut emissions. DTE's fully automated stationary analyzers have been tested in the industry, confirming that they are competitive with current laboratory analysis of process samples [4-7].

The portable DTE elemental analyzer discussed in this paper uses laser-induced breakdown spectroscopy (LIBS) to analyze the composition of the molten metal directly. LIBS is a spectroscopic technique that uses a high-energy laser pulse to generate a plasma on a sample surface and analyzes the spectral emissions from the generated plasma. LIBS can provide accurate, rapid, real-time multi-element detection for any type of material – solid, liquid, or gas [8-14]. It detects multiple chemical elements simultaneously, including light elements such as Li, B and Be. For many elements, detection limits of trace elements in the ppm range have been demonstrated in molten aluminium [4]. To date, however, the adoption of LIBS-based technologies in the industry has been limited and mainly focused on metal scrap sorting and identification with limited accuracy [11,15].

DTE supplies compact battery-powered analyzers, suitable for field measurements, thus creating the possibility for in-situ analysis of aluminium in reduction cells. The demand for in-situ analysis will only grow as industries drive their digital transformation towards integrating Industry 4.0. Within the aluminium industry, DTE's analyzers supplement aluminium chemistry results with advanced analysis where the chemical data from liquid metal is used to alert the operator, not only about deviated measurements but also possible future cell tap-outs or anode failures.

This paper's focus is on reporting the accuracy of DTE's portable liquid metal analyzers by comparing its performance with the traditional spark-OES technique. The implications for the future of chemical analysis in the potroom will also be discussed.

2. LIBS Attributes and Comparison with Traditional Spark-OES Method

LIBS and OES are two different plasma emission techniques that can be used to analyze aluminium samples. As mentioned above, LIBS uses a laser pulse to generate the plasma, whereas spark-OES uses a high voltage pulse source to excite plasma between an electrode and the sample. Both methods analyze spectrally resolved light emission from the plasma. Laser excitation makes the LIBS technique suitable not only for solid samples but also for liquids and gas. DTE's analyzers are specifically adapted to measure liquid metal as it gives numerous advantages over solid sample analysis. First, it helps to eliminate sample handling and sample preparation steps. These steps are tedious and may introduce measurement errors due to the segregation of elements or pores or cracks forming during pouring and solidification of the sample, contamination of samples from the molds or during preparation, and mix-up of samples. Second, eliminating the above steps also removes some of the safety hazard issues related to manual sample handling and transport. The third and most significant advantage is that it enables frequent real-time measurements with immediate feedback. This helps to deliver valuable intelligence through regular monitoring of impurity elements, thus improving cell operations. In contrast, conventional potroom samples are usually collected in sets and analyzed with some hours delay or more, depending on how loaded the laboratory is. Consequently, the condition of the cells can be very different from the conditions that analyzed samples represent and may no longer valid, especially for cells that are close to failure. Therefore, immediate chemical results can contribute to an improvement in cell operation as the response time is reduced from hours to seconds. A profitability analysis for real-time measurements in aluminium plants is discussed elsewhere in these proceedings [17].

As an initial step and using chemical analysis data alone, implementing logistic regression and random-forest methods, it was found that more than 25 % of cathode failures could be predicted with a 2-month time horizon, increasing to close to 80 % of cathode failures predicted with a 12-hour time horizon (see Figure 6). Prediction accuracy will be further improved by including additional physical data collected during cell operations, such as cell age, copper bar temperature, and other process variables that enhance prediction. Further details of the machine learning models and their implementation on real-time data will be presented elsewhere, including the correlation between different chemical species on one hand and failure modes and prediction horizons on the other.

6. Conclusion

DTE's portable elemental analyzer has been shown to deliver immediate chemical analysis of Fe, Si and Cu in molten aluminium from reduction cells, correlating well with OES analysis of conventionally extracted solid samples. Deployment of portable analyzers for potroom control hold great promise not only for real-time chemical analysis, but also as a predictive tool for potroom operation.

7. Acknowledgements

The authors gratefully acknowledge Rio Tinto ISAL for the collaboration and permission to publish the measurement data. Special thanks to Baldur Malmberg, leader of potroom process control at Rio Tinto ISAL for his expertise and fruitful discussions.

8. References

1. Morten Sørli, Harald A. Øye, *Cathodes in aluminium electrolysis*, 3rd Edition, Dusseldorf, Aluminium-Verlag, 2010, 662 pages.
2. Wayne R. Hale, Improving the useful life of aluminum industry cathodes, *JOM* 41, no. 11 (1989), 20-25.
3. Marilou McClung, and Zerkle Ron, Autopsy procedures and results at Century Aluminum of West Virginia, *Light Metals* 2004, 213-218.
4. Sveinn Hinrik Gudmundsson et al., Quantitative in-situ analysis of impurity elements in primary aluminum processing using laser-induced breakdown spectroscopy, *Spectrochimica Acta Part B: Atomic Spectroscopy* 158 (2019): 105646.
5. Sveinn Henrik Gudmundsson, Jon Matthiasson, and Kristjan Leosson, Quantification of trace elements in molten aluminum with randomized impurity concentrations using laser-induced breakdown spectroscopy, *OSA Continuum* 3, no. 9 (2020), 2544-2552.
6. Sveinn Hinrik Gudmundsson, Jon Matthiasson, and Kristjan Leosson, Accurate real-time elemental (LIBS) analysis of molten aluminum and aluminum alloys, *Light Metals* 2020, 860-864.
7. Sveinn Hinrik Gudmundsson, Halldor Gudmundsson, and Kristjan Leosson, Automated chemical analysis of liquid aluminum for process control, *Light Metals* 2021, 758-762.
8. D.A. Rusak, B. C. Castle, B. W. Smith, and J. D. Winefordner, Fundamentals and applications of laser-induced breakdown spectroscopy, *Critical Reviews in Analytical Chemistry* 27, no. 4 (1997), 257-290.
9. Leon J. Radziemski, *Lasers-induced plasmas and applications*, CRC Press, 2020.
10. Vahid Majidi, and Martha R. Joseph, Spectroscopic applications of laser-induced plasmas, *Critical Reviews in Analytical Chemistry* 23, no. 3 (1992), 143-162.
11. T. L. Thiem, R. H. Salter, J. A. Gardner, Y. I. Lee, and J. Sneddon., Quantitative simultaneous elemental determinations in alloys using laser-induced breakdown spectroscopy (LIBS) in an ultra-high vacuum, *Applied spectroscopy* 48, no. 1 (1994), 58-64.

12. A. Ciucci, Michela Corsi, Vincenzo Palleschi, S. Rastelli, Antonio Salvetti, and Elisabetta Tognoni, New procedure for quantitative elemental analysis by laser-induced plasma spectroscopy, *Applied spectroscopy* 53, no. 8 (1999), 960-964.
13. Elisabetta Tognon, Gabriele Cristoforetti, Stefano Legnaioli, and Vincenzo Palleschi. Calibration-free laser-induced breakdown spectroscopy: state of the art. *Spectrochimica Acta Part B: Atomic Spectroscopy* 65, no. 1 (2010), 1-14.
14. David A. Cremers, and Leon J. Radziemski, *Handbook of laser-induced breakdown spectroscopy*, John Wiley & Sons, 2013.
15. Vincenzo Palleschi, If laser-induced breakdown spectroscopy was a brand: some market considerations, *Spectrosc. Eur.* 29 (2017), 2.
16. Sveinn Hinrik Gudmundsson, Birna Björnsdóttir, and Kristjan Leosson, Instant monitoring of aluminum chemistry in cells using a portable liquid metal analyzer, *Light Metals* 2021, 491-494.
17. Berglind Höskuldsdóttir, Karl A. Matthiasson, and Pall Jensson, Profitability increase in aluminium smelter potroom using real-time elemental analysis from Liquid Metal based on LP-LIBS, *Proceedings of 39th International ICSOBA Conference*, Virtual, 20-25 November 2021, Paper AL37, *Travaux* 50.