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INDUSTRIAL IMPLEMENTATION OF PYROLIBS FOR CONTINUOUS HOT METAL CHEMISTRY MEASUREMENT

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The PyroLIBS system is a next generation technology for pyrometallurgy, capable of continuous and instant measurement of chemical compositions for molten materials. The present paper presents the early results of its first industrial implementation in a blast furnace runner, for continuous hot metal analysis.

KEYWORDS: BLAST FURNACE IRONMAKING – AI – HOT METAL SILICON MEASUREMENT – PROCESS CONTROL

INTRODUCTION

Hatch has partnered with the National Research Council of Canada to develop and commercialize PyroLIBS, a probe capable of providing continuous, direct, and real-time measurement of molten material chemistry. The applications of interest are harsh pyrometallurgical processes above 1000 °C, including a variety of applications in the iron & steel value chain. Coupled with the appropriate process control philosophy, PyroLIBS is expected to provide significant improvements to a variety of processes, in the form of productivity increases, material and energy savings, and more. This paper provides an overview of the first industrial application of the PyroLIBS system in an operating blast furnace runner.

BACKGROUND

There is a significant interest in advanced process models, particularly those powered by AI, to improve modern pyrometallurgical process performance. However, these models are only as good as the information they are fed. As pyrometallurgical vessels are essentially large chemical reactors, one area where accurate and timely information is useful is in the determination of chemical compositions, particularly of molten metal and slag. However, the measurement of molten material is challenging, owing to harsh process conditions where temperatures on the order of 1500 °C are often encountered [1].

Despite these challenges, several methods exist to measure molten material composition. The most common is manual sampling and analysis, where a molten sample is cooled, prepared, and measured using standard laboratory equipment. This method has several drawbacks. Firstly, it is not instant, as it typically takes several minutes [2] to a few hours for a sample result to be known, depending on available plant resources, and the relative importance of such a measurement for operations. Secondly, the measurement is not continuous, as operators must choose discrete points in time to take samples. Thirdly, manual sampling exposes workers to extreme conditions to collect samples, posing safety risks.

Other common methods for molten chemistry measurements use indirect means. These methods track a proxy that is simpler to measure, such as temperatures or off-gas compositions, and relate the proxy back to the molten material, using known relationships [3]. The benefit of such an approach is that a real-time data stream can be established. However, such methods can only measure certain elements, as not all elements will have a link to a proxy. Further, as these methods often rely on assumptions to link proxy and measurement, they can lack accuracy compared to direct measurement. For example, linking an off-gas proxy with a molten metal

measurement, through a thermodynamic equilibrium assumption, introduces error by ignoring kinetics.

There does exist a technique that can provide direct and real-time measurement of molten material composition: laser-induced breakdown spectroscopy (LIBS). The basis of LIBS is well known: a laser is focused on a very small target for a short period of time, momentarily heating the molten material to very high plasma temperatures. As the plasma cools down, it emits radiation, which is analyzed like other spectroscopic methods [4]. While LIBS itself is well established in industry, especially for analysis of solid materials, its application to molten materials remains a technological frontier.

The literature on molten LIBS measurement contains a variety of approaches. In some, the laser pulse is directed on the top surface of a melt, which is advantageous as it is relatively easy to create a stable plasma on a flat surface, allowing for simple measurement [5]. Such approaches are not ideal, as even if slags and other floating materials are cleared away, microscopic oxides can still form on the melt surface, leading to non-representative results. Since each laser shot only vaporizes a tiny fraction of the melt into a plasma state, such relatively small oxide layers, which may be invisible to the naked eye, could still add significant errors to the measurement. To alleviate this issue, other approaches conduct the LIBS measurement through a lance filled with an inert gas and dipped into the melt [6]. Many of these lance-based methods deliberately control the pressure inside the lance to keep the measurement surface flat, allowing for simpler and more steady plasma generation. Unfortunately, such techniques are also not ideal, as melts can be very heterogeneous, and measuring a stagnant surface at the tip of the lance (e.g., a static inclusion) will fail to adequately represent the overall bulk chemistry in a timely manner.

Due to the shortcomings with other molten LIBS methods, researchers at the National Research Council of Canada (NRC) pioneered a novel approach [7]. As shown in Fig.1, the lance-based approach is modified by ensuring that the lance is bubbling, and not stagnant. While more challenging from a LIBS perspective, this approach allows for the measurement surface to be rapidly refreshed, resulting in a faster and more accurate measurement of the full melt chemistry considering all its heterogeneity. Following development of the bubbling LIBS approach, the NRC then partnered with Tecnar to commercialize the technology for molten materials up to 1000 °C. Over the last 20 years, Tecnar has installed over 70 Galvalibs units worldwide [8]. More recently, NRC and Hatch partnered to commercialize the PyroLIBS probe for molten materials above 1000 °C, with a special focus on the iron & steel flowsheet.

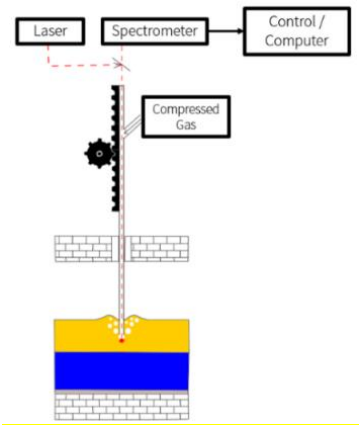

Fig.1 – The NRC's bubbling lance LIBS method, used by PyroLIBS.

Value to Blast Furnace Ironmaking

While several benefits exist for the real-time chemical composition measurement of blast furnace hot metal and slag, the most important control element is the hot metal silicon, as this is a well-known indicator of the blast furnace thermal state. Every blast furnace operator plans to reduce fuel consumption, principally metallurgical coke, as much as possible. In doing so, the operator must maintain a residual silicon content in the hot metal to be confident that the blast furnace hot metal and slag will always be molten. Decisions to

control fuel and coke consumption are made based on the hot metal temperature (an indicator of the physical condition of the furnace), and the hot metal silicon (an indicator of the chemical status of the furnace). Hot metal silicon must be reduced carefully and controlled precisely, as silicon content is directly related to the reduction of heat input to the furnace, which can cause a chilling hearth if the furnace is under fueled [1].

Each 0.1% reduction in hot metal silicon is estimated to save approximately 5M USD/year for a hypothetical blast furnace with 2M tpy of production, assuming 4kg/tonne-hot-metal savings in coke at the blast furnace [1], 3.8 kg/tonne-hot-metal reduction in scrap required at the BOF [9], and 9.2 kg/tonne-hot-metal reduction in flux required at the BOF [9]. Note: this estimate assumes calculation parameters for a typical operation, not parameters that are specific to any particular operation, including the operation at which this probe was piloted.

Real-time measurement will not improve the blast furnace process without a good understanding of how the enhanced data will be used to achieve better control, highlighting the importance of pairing the probe with an appropriately advanced process control or AI system [1]. This is further addressed in the Discussion section.

BLAST FURNACE PILOT AND RESULTS

To demonstrate the capabilities of PyroLIBS to measure hot metal chemistry, an initial proof of concept test was conducted at lab scale. Following this lab scale testing, in-plant piloting was completed on an operating blast furnace consisting of two phases: the lance testing phase, and the full probe piloting phase.

Lance Testing Phase

A variety of lance materials were tested over the course of several months, with the goal of determining a minimally viable lance design. Fig.2 shows representative photos of the lance testing phase.

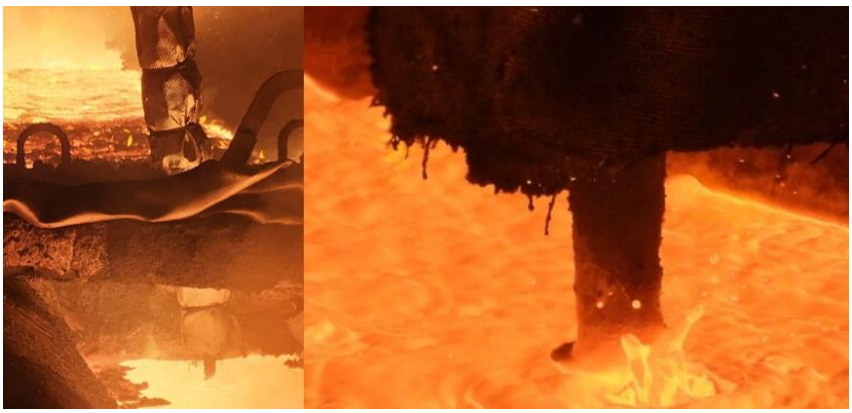

Fig.2 – The PyroLIBS bubbling lance being tested during the lance testing phase.

The minimally viable lance has several requirements. It must:

1. Be able to withstand repeated thermal shocks from insertion into, and removal from, the ~1500 °C hot metal, with essentially no pre-heating, other than what is required to drive off residual moisture, and without using water cooling.
2. Last at least one week without operator intervention, and inserted into the hot metal 50% of this time.
3. Be highly impermeable to prevent contamination of the argon gas used in the LIBS measurement.
4. Not clog during operation.
5. Withstand reasonable amounts of mechanical stress, which may be expected during operation.

Through the lance testing phase, a suitable lance material was found to meet all the minimum requirements.

Full Probe Piloting Phase

Following the lance testing phase, the full probe piloting phase was conducted to demonstrate measurement of hot metal chemistry. The probe was installed at one iron trough of an operating blast furnace, above the

fume collection hoods, with a lance inserted into the hot metal.

The instrument consists of a Q-switched Nd:YAG pulsed laser, providing 300 mJ of energy per pulse, at a wavelength of 1064 nm. The radiation emitted by the plasma is collected by optical fibres and analyzed using commercially available spectrometers. Specifically for the measurement of Si I at 288.16 nm and Mn II at 293.31 nm, a Czerny-Turner spectrometer equipped with a 3600 line/mm grating and an intensified CCD camera was used. Measurement frequencies between 1 – 2.5 Hz were employed during the pilot.

The full probe piloting phase included two week-long campaigns, separated by a few months. During each campaign, the probe demonstrated the ability to withstand the high heat and dusty conditions while making continuous real-time measurements. The probe successfully operated for periods of up to 12 hours at a time, corresponding to the shift duration of the Hatch and NRC operators.

Manual Sampling Uncertainty Tests

The PyroLIBS measurements were compared to manual samples taken at the iron trough, and analyzed by the blast furnace operations team, using the normally utilized spark OES machine. In general, manual samples were taken every 5-10 minutes while the probe was in operation. The analysis of the initial set of manual samples taken during the pilot campaign suggested a large degree of measurement uncertainty.

To better understand this manual sampling measurement uncertainty, two tests were conducted, separated by a few months. For each test, samples were taken from the same location as quickly as possible (or 'simultaneously'), with ~15-30 seconds in between each sample as the sampling rod was swapped. In Test 1, 10 samples were taken from the iron trough, and 10 samples were taken from the downstream torpedo car 'simultaneously'. In Test 2, 16 samples were taken from the iron trough within ~4.5 minutes. Each sample was then analyzed via spark OES by the blast furnace operations team. In theory, if there were no sample preparation & analysis errors (i.e., human or machine error), if the samples were truly taken simultaneously, and if the melt was completely homogeneous, all of the samples should have had the same composition.

As shown in Fig.3 for hot metal silicon, the tests showed a variance in the compositions, compared to the mean. When conducting the statistical analyses, this variance, hereafter called the 'manual sampling uncertainty' was estimated at up to $\pm 2\sigma = \pm 0.05\%$ for 95% of data and $\pm 3\sigma = \pm 0.08\%$ for 99.7% of the data, on an absolute silicon % basis. Even though the testing was imperfect, and the sample size is small, the variation points to limitations inherent to manual sampling and analysis accuracy. One known factor that can have a significant impact on manual sampling accuracy is precise sample preparation, which is known to be particularly challenging for hot metal samples. Difficulty in precise sample preparation hence tends to be a source of human error that increases measurement uncertainty. The Discussion section elaborates on the implications of this finding for the ability to improve blast furnace control using real-time and direct chemistry measurement, compared to manual sampling and analysis.

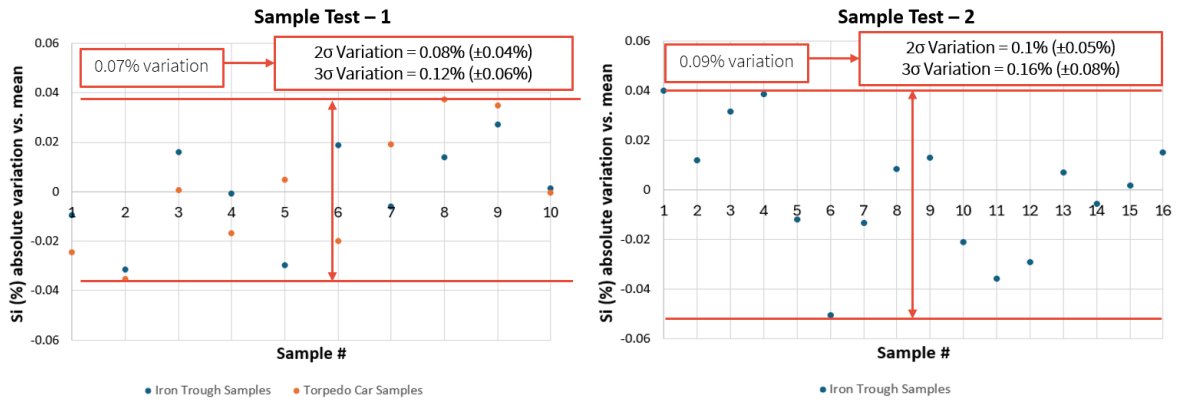

Fig.3 – Simultaneous sample testing to understand manual sample accuracy; absolute Si (%) discrepancy with respect to the mean is reported for each sample. 2σ and 3σ variances account for an estimated 95% and 99.7% of data.

Probe Measurement Results

In Fig.4, the PyroLIBS hot metal silicon and manganese analyses are compared against the standard manual sample analyses by spark OES. On each plot, two green dashed lines represent the magnitude of the manual sampling uncertainty, described above. A strong correlation is observed between the PyroLIBS and spark OES results, and the remaining lack of correlation is within the bounds of the manual sampling accuracy.

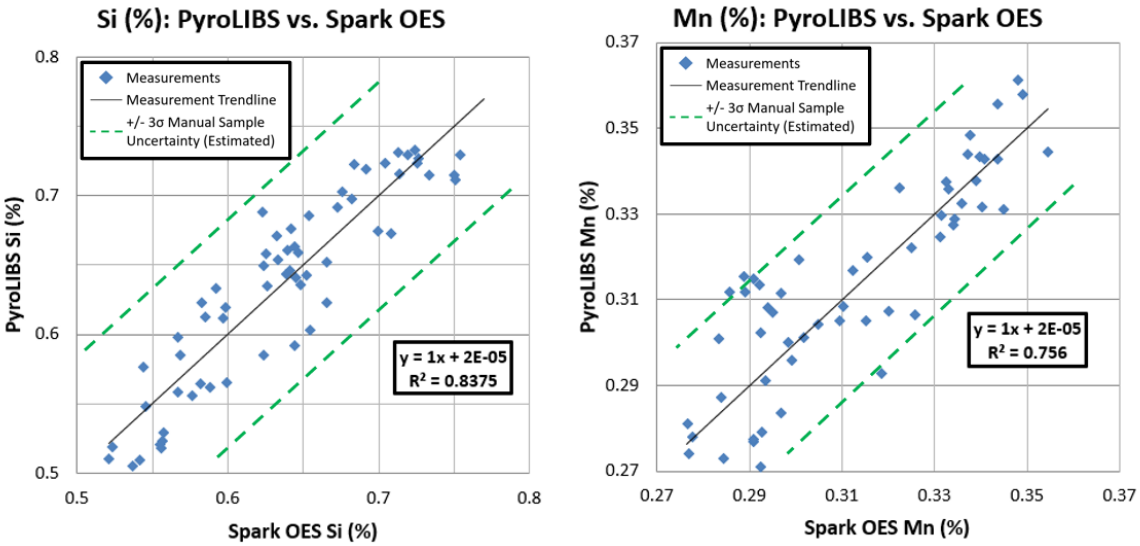

Fig.4 – PyroLIBS vs manual samples (analyzed via spark OES) for hot metal Si (left) and Mn (right).

In Fig.5, the measurements of hot metal silicon and manganese are compared over time for two sample casts during the measurement campaign. For PyroLIBS, each data point represents a 2-minute average of data. For the manual samples analyzed via spark OES, two results are provided by orange triangles and red dots. The orange triangles represent the routine manual samples taken at the torpedo car, every ~30 minutes. The red dots represent the samples taken at the iron trough for the purpose of the PyroLIBS pilot only, and are not routinely taken by operations.

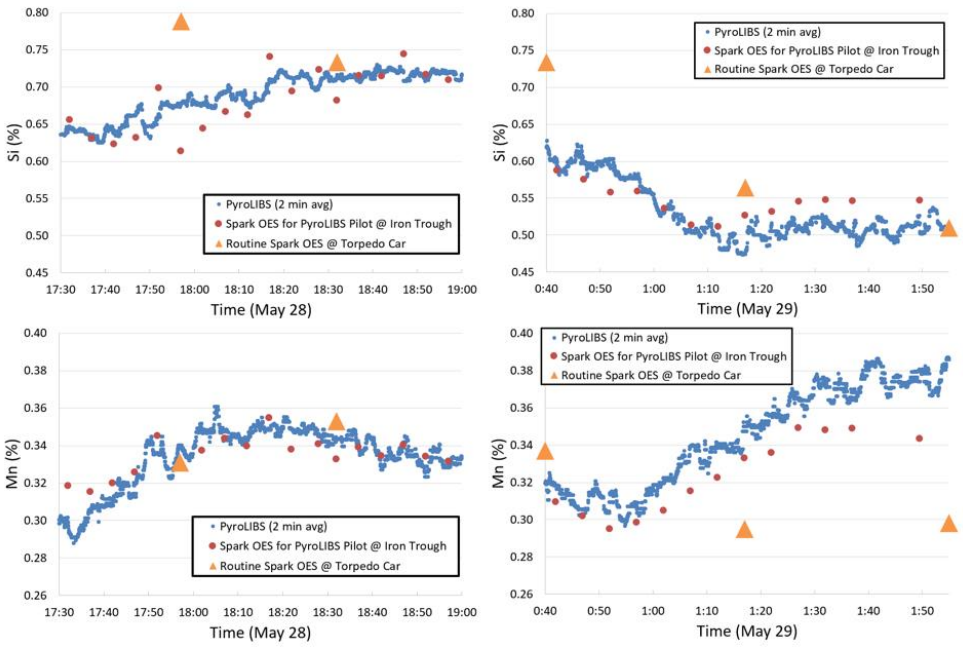

Fig.5 – PyroLIBS vs. spark OES measurements for hot metal silicon (top) and manganese (bottom) during two casts.

As shown in Fig.6, PyroLIBS was able to detect slag inclusions in the hot metal. The heat map represents the frequency of data points in each region, the Y axis shows the calcium signal, present only in the lime component of slag, and the X axis shows the silicon signal, present in both hot metal and slag. Most data points describe hot metal measurements with minimum calcium signal. Data emanating from the hot metal region tends to increase in both calcium and silicon signal at a roughly fixed ratio, representing the $CaO\text{-}SiO_2$ based slag inclusions.

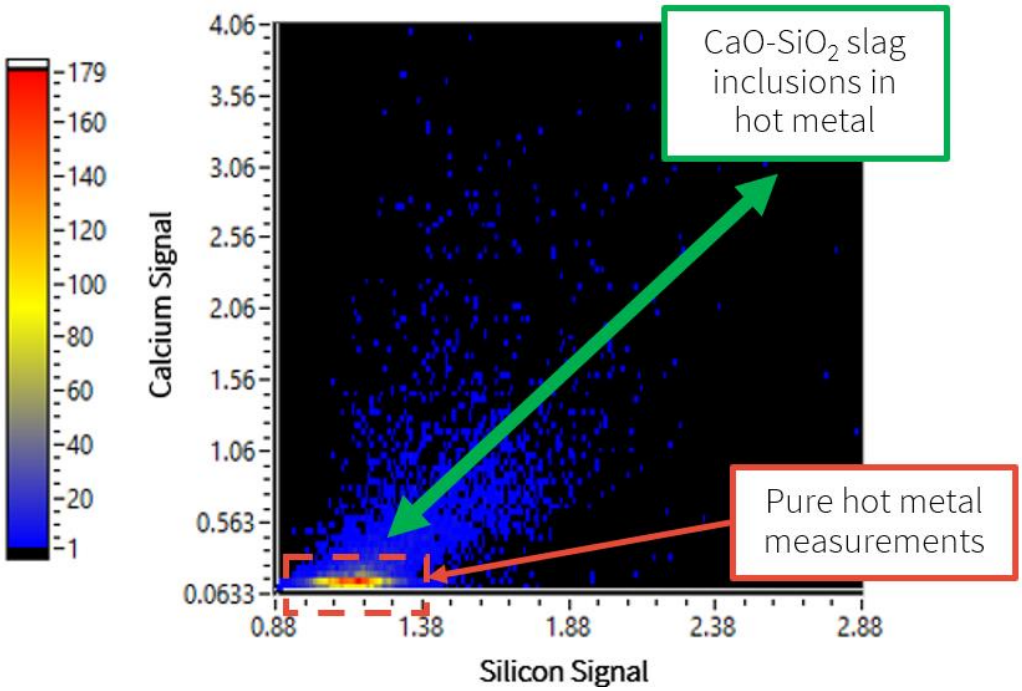

Fig.6 – Slag inclusions in the hot metal for one cast. The heat map represents the frequency of data in each region.

The scatter in the data is predominantly because each LIBS measurement analyzes an area, which may have a varying mix of slag and hot metal, based on the amount of material vaporized with each laser shot. Hence, the nature of the LIBS measurement will lead to scatter in the individual data, which is then reduced by taking a very high frequency of measurements, to fully characterize the melt.

Based on past studies, the size of slag inclusions that will make it past the skimmer block have a mean diameter of ~60 µm, with an upper bound of ~140 µm [10]. The typical size of the LIBS measurement is about 100-200 µm [4]. Although there is only a small amount of slag carry-over, given the high frequency of measurements, some individual data points inevitably have a high degree of slag signal. For this reason, it is anticipated that the measurement of slag chemistry can be done by the same probe, at the same location, by a statistical analysis of the laser shots related to slag inclusions. At present, there is not enough data to prove this conclusively, as the probe only encountered two zones of slag chemistry during the pilot (i.e., each of the two pilot weeks had a roughly constant slag chemistry, slightly differing from the other week). Hence, statistical analyses for the accuracy of the probe measurement vs. slag samples at this point is premature, as the correlation between two data points will always be perfect or zero.

DISCUSSION: BENEFITS OF REAL-TIME HOT METAL CHEMISTRY ANALYSIS

As previously noted, to achieve the desired benefits, real-time chemistry needs to be paired with the appropriate operator knowledge, advanced process control model and/or AI models. Benefits will be discussed here for each component of hot metal chemistry that can be measured.

Benefits of Real-Time Hot Metal Silicon Measurement

As noted earlier, every 0.1% reduction in hot metal Si is expected to provide approximately 5M USD/year in benefit, by decreasing blast furnace fuel consumption and carbon footprint, with additional savings at the BOF shop. This savings estimate uses calculation parameters for a typical blast furnace operation, not parameters that are specific to any particular operation. Real-time chemistry enables this careful reduction due to three important characteristics.

The first characteristic is the direct measurement on hot metal, which eliminates manual sampling uncertainty attributable to sample preparation challenges. The second characteristic is the continuous nature of the measurement, allowing for roughly 3 orders of magnitude more sampling than current best practice using manual sampling (i.e., 1-2 measurements per second vs. 1 manual sample every ~30 minutes). This massive increase in sampling frequency further reduces measurement uncertainty, as it can fully account for variations due to both melt heterogeneity, and the natural variations of hot metal silicon throughout the cast [11]. The third characteristic is the instantaneous nature of the measurement, which allows for much faster feedback control for fuel rate adjustments, at the blast furnace tuyeres. These adjustments impact hot metal silicon on the order of minutes, compared to changes made to coke charges at the top of the blast furnace, which take on the order of hours to impact the hot metal chemistry.

Since hot metal silicon control at the blast furnace (aided by operator judgement, advanced models etc.) relies at the most fundamental level on hot metal silicon measurement, any reduction in the uncertainty of that base measurement provides room for further process optimization that was previously unattainable. Compared to best practice, real-time direct measurement is believed to allow for a minimum 0.1% reduction in hot metal silicon. This estimation is based on the elimination of manual sampling uncertainty, as described earlier, as well as the additional benefits attributable to the continuous and instant assessment of hot metal silicon. Operating risk is also reduced as operators can react much faster to problematic conditions, reflected by changing hot metal silicon levels, such as those conditions that may cause a chilling hearth and problems removing slag and hot metal from the blast furnace.

The full range of benefits can be realized by forwarding the chemistry data to the steel shop, averaged for each torpedo car, and now with reduced measurement uncertainty. This allows for better flux and scrap addition at the BOF, as well as potentially alleviating slopping issues for some operations [1].

Other Benefits

With real-time manganese measurement, sampling uncertainty can be reduced, allowing for further optimization of where manganese should be added to the process, at the BF as low-cost Mn containing ore or at the BOF as higher cost ferro-manganese. With the measurement of slag inclusions in the hot metal, skimmer block and hot metal dam performance can be systematically assessed, and refractory maintenance frequency better optimized to maximize hot metal and slag separation [10].

Future Capabilities

As described earlier, there is a potential to measure slag chemistry (CaO%, SiO2% etc.) via the analysis of hot metal slag inclusions, although more data is needed before this can be conclusively stated.

Sulfur measurement is also feasible, allowing for improved blast furnace control and input to subsequent hot metal desulfurization before steelmaking [1]. The probe's estimated sulfur detection limit, based on analysis of solid samples, is approximately 650 ppm. Relatively simple means exist to increase the LIBS signal, thereby potentially reducing the detection limit to ~200 ppm, which is at a level of interest to blast furnace operators [1]. For example, by using more accurate spectrometers compared to the equipment used by the probe, and by reducing the distance between the probe head and the hot metal, as the LIBS signal is proportional to the inverse square of this distance [4].

CONCLUSION

The performance of the PyroLIBS probe has been demonstrated in the blast furnace runner system, for the real-time and direct measurement of hot metal silicon, manganese, and slag inclusions. Given the measured uncertainty inherent in the manual sampling process, a hot metal silicon reduction of at least 0.1% appears possible with the addition of real-time chemistry measurement, compared to current best practices. Other benefits include the ability to optimize manganese additions, and the ability to track slag inclusions for monitoring of runner system wear and improving refractory maintenance.

With the successful completion of the pilot, the next step is the design and implementation of the first commercial system, for use by operations, which will be optimized based on the findings of the pilot.

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