

# Real-time phosphorous measurement using a sublance probe

*The use of sublance technology has reduced the need to wait for an end blow steel carbon samples before tapping the BOF vessel. However, as steel phosphorus specifications continue to tighten and use of higher phosphorus iron ores increases, the need to wait for a steel phosphorus sample can still cause delays to tapping. A new approach to online phosphorus determination using a combination of sublance technology and the Healy chemical equilibrium formula has been successfully developed.*

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Controlling phosphorous levels during the steelmaking process has always been difficult. With the increased use of iron ores containing high phosphorous, the measurement of phosphorous at the end point in BOF steelmaking continues to be a subject of interest because of its impact on steel quality. BOF slag is complex in nature and contains several oxides like CaO, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, MgO, MnO and FeO. Towards the end of the blow the kinetics of some reactions slows down such that slag composition approaches a kind of pseudo-equilibrium with the metal. Thus, application of thermodynamic models alone for direct estimation of phosphorous distribution does not yield sufficient reliable information for start tapping decisions.

This paper describes a new measurement technology, based on sublance TSO measurement. During a period of three years, extensive development was carried out in steel plants that were in normal operation.

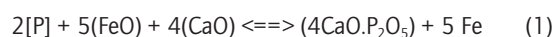
## METALLURGICAL BACKGROUND

Many models have been developed to predict the end point phosphorous content on the basis of thermodynamic models<sup>[1]</sup>, regression analysis, neural networks or even using purely empirical equations<sup>[2]</sup>.

One thing they all have in common is the Healy formula, which has always been the leading basis for determining the phosphorous content of both the slag and the steel bath.

As equilibrium cannot be reached the formula has proven to be not accurate enough for the purpose of online calculation in BOF steelmaking practice. Therefore, some other variables originating from sublance measurement or calculated by the Level 2 process control model have been added to this calculation to enhance the accuracy of phosphorus determination.

The original Healy formula<sup>[3]</sup> is based on the following equilibrium equation:



This can be transformed to<sup>[4]</sup>:

$$\log \left\{ \frac{(\%P)}{[\%P]} \right\} = \frac{22350}{T} + 0.08(\%CaO) + 2.5 \log(\%Fe) - 16.0 \quad (2)$$

where:

[%P] is mass % of P in metal

(%P) is mass % of P in slag

(%Fe) is mass % of Fe in slag

(%CaO) is mass % of CaO in slag

T is temperature in Kelvin.

As can be seen from this expression, for an accurate online phosphorous determination, the temperature of the steel, which can be measured easily by means of a sublance, and the CaO and Fe (or FeO) content of the slag need to be determined.

## CaO AND FeO

The CaO content of the slag is taken from the Level 2 process control model, which calculates the actual CaO content based on real process data. To determine the FeO content of the slag accurately, a new FeO model was developed. This sub-model is based on slag sample analysis, combined with signals coming from a specially designed oxygen cell and with other important input variables from the Level 2 process control model, such as CaO and MgO content of the slag. This model should be trimmed and kept up to date by feeding it regularly with new slag data.

## PHOSPHOROUS FORMULA

This 'measured' FeO is then fed to a newly developed P-formula. This formula (actually a trimmed process control model) is derived from analysis of extensive plant data (hot metal data, steel analysis) combined with Level 2 process control model data. The formula still relies heavily on Healy, as described above, but is enhanced through addition of parameters from the Level 2 process control model.

## TECHNOLOGY DEVELOPMENT

Although the first attempts were made to use the oxygen activity signals from the end of blow TSO probe (temperature, sample, oxygen) measurement over a decade ago, a new team of engineers took up the challenge to go beyond existing technologies and develop a real time phosphorous measurement.

Key aspects of the measurement, such as the oxygen sensor, the measurement cycle, the data recording and data processing, were subsequently optimised for phosphorous determination. This was done under two strict conditions: that the TSO performance for carbon and end temperature control should not be compromised and that during plant trials, the phosphorous measurement should not influence normal steelmaking operation in any way.

From the beginning it was apparent that the standard oxygen sensor, as applied for carbon and temperature measurement, had to be improved to give a better and more stable sign of oxygen activity in the slag. An optimised oxygen sensor now consists of a newly designed reference electrode and is made of a specific cold-rolled steel grade. This results in a stable signal in slag, even though the sensor itself was meant to function in the steel bath.

Referring back to Healy, it was clear to the development team that more data was required for phosphorous measurement than the oxygen activity alone. The DIRC measurement computer was modified, this time through adding functionalities to the software. Level 2 data collection and storage capability were also added.

The most complex step was to convert the process data into information and to find a suitable way of presenting the measured phosphorous. The first step was to extract key components of the full-size Danieli Corus Level 2 process control model. These components were combined into a miniature process model, focused on calculating phosphorous. This P-model was sent to the DIRC measurement computer, allowing it to calculate the phosphorous from TSO measurement data in real time.

## DEVELOPMENT RESULTS

First results of the development work were an optimised sublance measurement cycle and an improved oxygen sensor. With the extended Healy relationship adding ▽

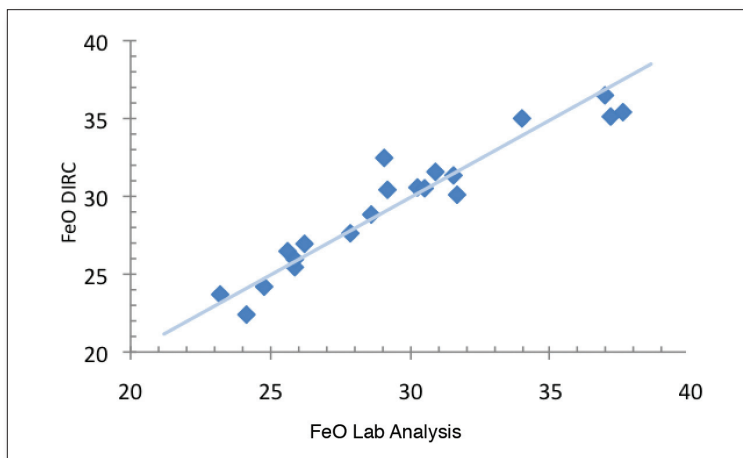


Fig 1 FeO calculated by DIRC from oxygen activity vs FeO from laboratory analysis at Ma'anshan, China

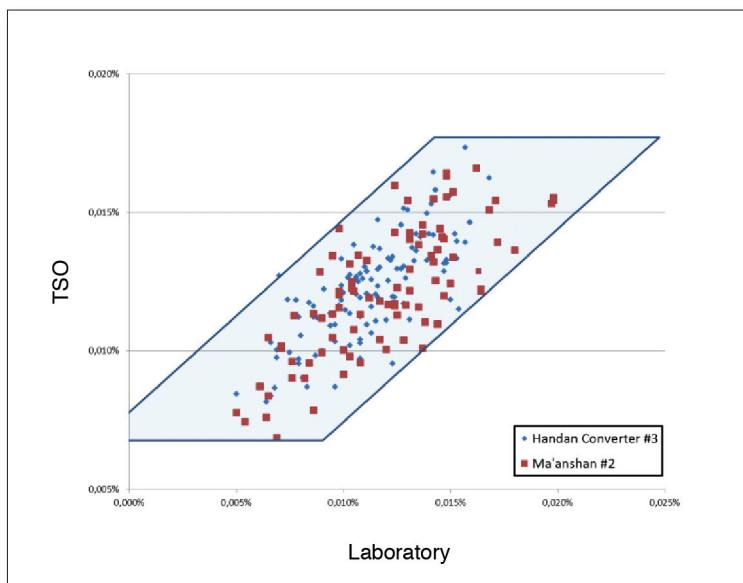


Fig 2 Phosphorous content measured by sublance TSO v laboratory analysis of steel sample

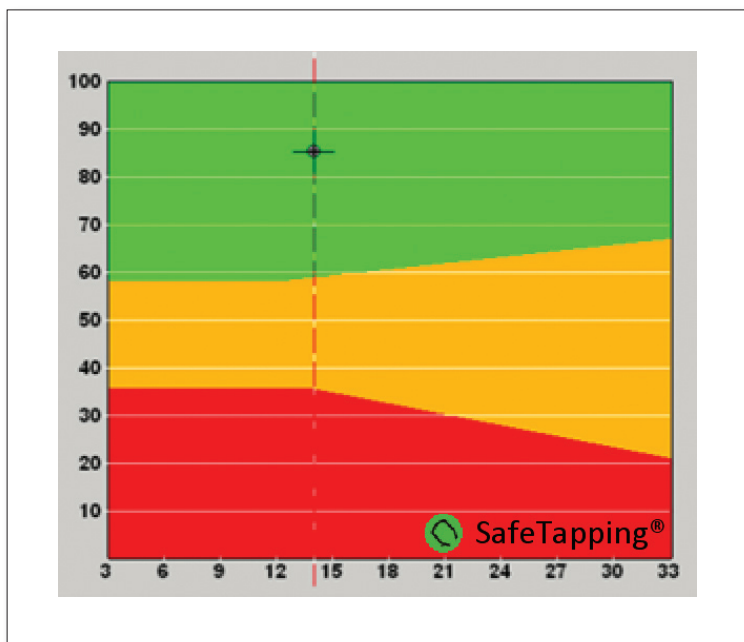


Fig 3 Safe tapping graph

oxygen activity from sublance and real-time Level 2 process data (such as hot metal composition and material additions), phosphorous can be measured in real time using the oxygen activity data from the end-of-blow TSO measurement.

The excellent relationship between the measured FeO (through slag analysis) and the calculated FeO (oxygen activity by DIRC) is shown in Figure 1. With a deviation of only 1-2%, this FeO relationship acts as the backbone for the phosphorous measurement.

In Figure 2, the experimental results from field trials in two Chinese steel plants are shown. It should be noted that both steel plants made no alterations to their normal converter operation to develop more favourable conditions for phosphorous measurements and no precautions were taken, with respect to converter addition material quality, quantities or other process control parameters.

In both plants it was possible to limit the standard deviation of the measurement to 20ppm with a phosphorous content in the steel bath of 300ppm.

## APPLICATION OF SUBLANCE-BASED PHOSPHOROUS MEASUREMENT

The final step in the development of the real-time

phosphorous measurement was to assist the operator in the converter control room to decide whether or not to start tapping the heat via the addition of a decision support system. Rather than showing the measured phosphorous content on the operator screen and letting the operator interpret the data, it was decided to present the phosphorous content through a newly developed concept called SafeTapping®.

SafeTapping is a graphical information tool that informs the operator through a multi-coloured graph if it is safe to start tapping the heat. After each TSO measurement, a marker will be shown on the SafeTapping graph, as shown in Figure 3. On the horizontal axis, the maximum allowed phosphorous content is shown. The dashed line indicates the maximum phosphorous of the current steel grade.

On the vertical axis, the probability that the actual phosphorous content is lower than grade maximum is shown. The higher the percentage, the higher the probability that it is safe to start tapping.

When the marker appears in the green zone, it means that current phosphorous content is below the maximum content predefined by the steel grade. Figure 3 shows the marker at 85%, indicating that the current produced heat can be tapped safely.

In the event that the actual phosphorous content exceeds the grade maximum, the marker will appear in the red zone. Without any further delays, caused for instance by waiting time for laboratory results, the operator can decide with a short glance whether he can start tapping or if it is necessary to initiate a short re-blow aimed at a further phosphorous reduction in the steel bath.

A marker appearing in the orange area means it is advisable to wait for the actual laboratory results before taking a decision. **MS**

## REFERENCES

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- [4] R Boom and B Deo, *Fundamentals of Steelmaking Metallurgy*, Brady Publishing, 1993.

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