ON-LINE PHOSPHOROUS MEASUREMENT IN BASIC OXYGEN STEELMAKING[1]

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Abstract

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 end point in BOF steelmaking continues to be a subject of interest because of the impact of Phosphorous on steel quality. BOF slag is complex in nature and contains several oxides like CaO, SiO2, P2O5, MgO, MnO, and FeO etc. Towards the end of blow the kinetics of different reactions slows down such that slag composition approaches a kind of pseudo equilibrium with metal. Thus, application of (thermo-dynamical) models alone for direct estimation of Phosphorous distribution does not yield sufficient reliable information for start tapping decision. This memo describes a new measurement technology that was developed by DC for its sublance customers. The Phosphorous measurement is based on the TSO end of blow measurement, but was further enhanced over a four year development period. As final step in the technology development, a new user friendly graphical representation was created that facilitates the decision making of the converter operator at the end of heat.

This technology development was carried out in several steel plants that were in normal operation.

Key words: Phosphorous; Converter; Measurement; Sublance.

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1 METALLURGICAL BACKGROUND

Many different models are developed to predict the end point Phosphorous content on the basis of thermodynamic models, with various degrees of regression analysis, neural networks or even using purely empirical equations.
One thing they all have in common is the Healy formula, which has always been leading and the basis for determining the Phosphorous content of both the slag and the steel bath.
Due to equilibrium that cannot be reached, the formula has proven not to be accurate enough for the purpose of online, in BOF steel making practice, measuring of phosphorous. Therefore, in the here presented method some other variables originating from the sublance measurement or calculated by the level 2 process control model are added to enhance the accuracy of the measuring method.
The original Healy formula is based on the following equilibrium equation:

$$2[P] + 5(FeO) + 4(CaO) \Longleftrightarrow (4CaO.P2O5) + 5\,Fe \qquad (1)$$

This can be transformed this to:

$$\log\{\frac{(\%P)}{[\%P]}\} = \frac{22350}{T} + 0.08(\%Cao) + 2.5\log(\%Fe) - 16.0 \qquad (2)$$

With:
[%P] is mass % of Phosphorous in metal
(%P) is mass % of Phosphorous 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 Phosphorous measurement next to the temperature of the steel, which can be measured easily by means of a sublance, also the CaO and Fe (or FeO) content of the slag need to be determined online.

1.1 CaO and FeO

For the here presented method, 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 and added to the measurement. This sub-model is based on slag sample analysis, combined with signals coming from a special designed oxygen cell and with other important input variables from the Level 2 process control model, as CaO and MgO content of the slag. This model should be trimmed and kept up to date by regularly feeding it with new slag data.

1.2 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.

2 DEVELOPMENT RESULTS

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

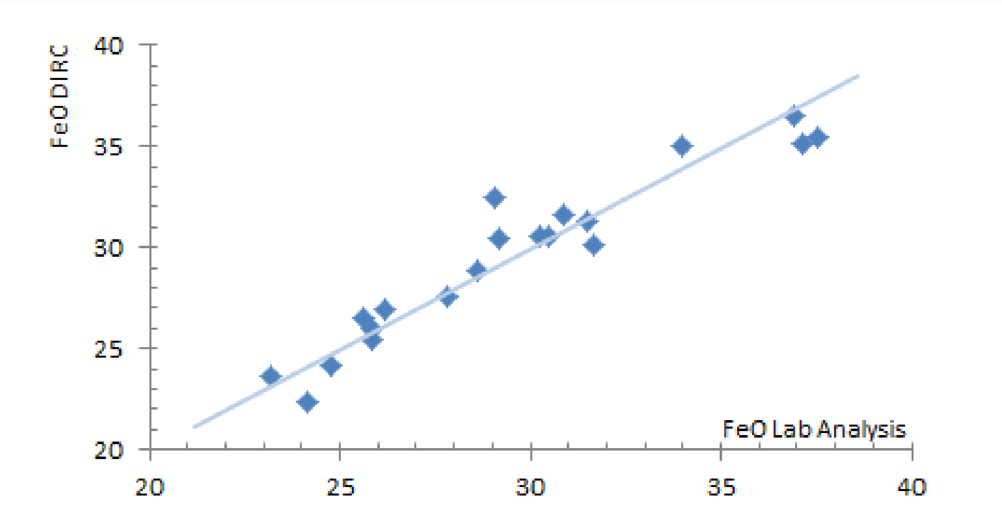

Figure 1. FeO calculated by DIRC from oxygen activity vs. FeO from laboratory analysis at Ma'anshan, China.

In Figure 2 the results from recent measurements from Maanshan Steelplant #4 are shown. It should be mentioned that Maanshan steel plant did not make any alterations to their normal converter operation to come to more favourable conditions for Phosphorous measurements. No precautions were taken, with respect to converter addition material quality, quantities or other process control parameters.
It was possible to limit the standard deviation of the measurement to 24.6 ppm with a Phosphorous content in the steel bath of <300 ppm.

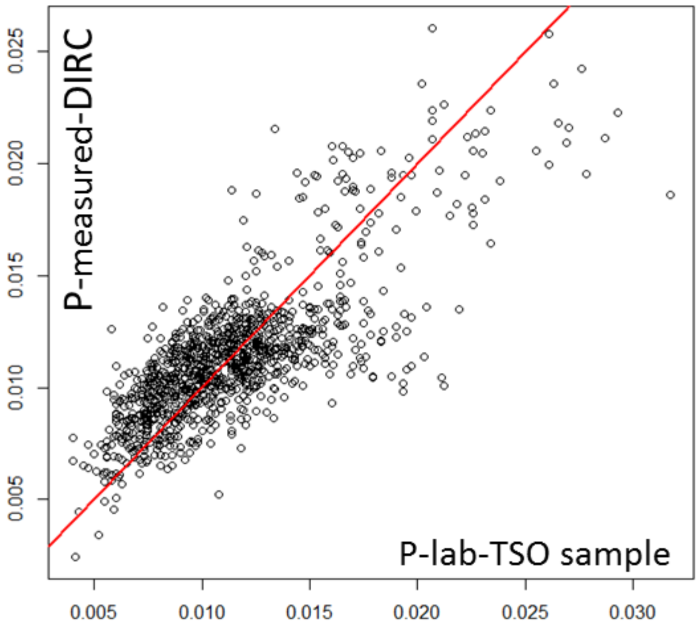

Figure 2. Phosphorous content measured by DIRC versus laboratory analysis of steel sample from TSO.

3 APPLICATION OF SUBLANCE BASED PHOSPHOROUS MEASUREMENT

Danieli Corus has developed a graphical representation of the TSOP measurement that will assist the operator in the converter control room, in his decision making whether to start tapping the heat or not. Rather than only showing the measured Phosphorous content on the operator screen and let the operator interpret the data, the Phosphorous measurement is shown in the “SafeTapping®” mode.

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

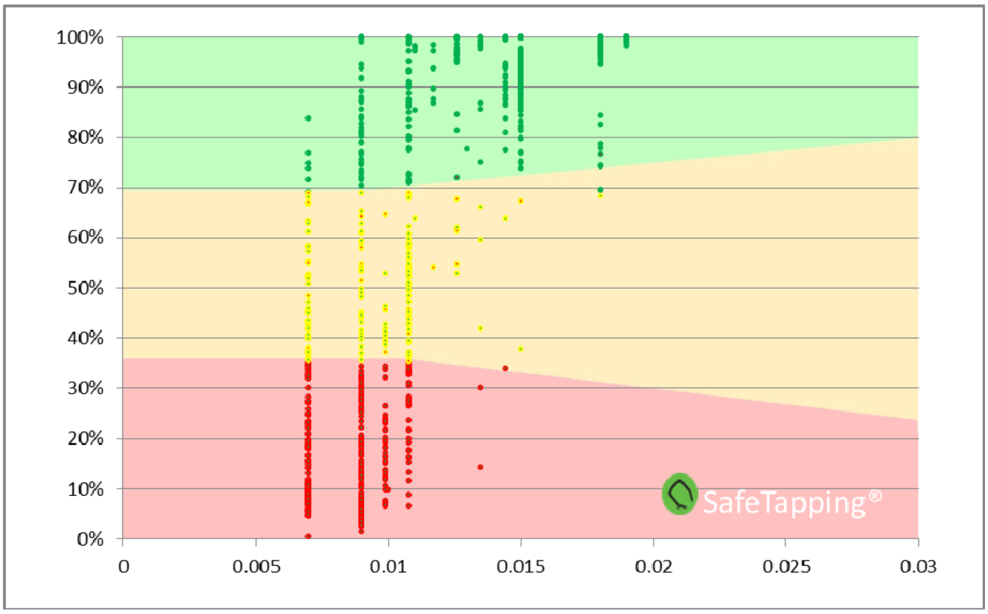

Figure 3. SafeTapping® information graph showing the probability to safely start tapping the finished heat while remaining under the maximum allowed Phosphorous level.

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 Phosphorous content that is pre-defined by the steel grade.
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 necessary to initiate a short re-blow aimed at a further Phosphorous reduction in the steel bath.
A marker appearing in this orange area, means it is advised to wait for the actual laboratory results before taking a decision.

4 SAFETAPPING® IN MAANSHAN

As part of the TSOP measurements in Maanshan steel plant #4, SafeTapping® performance was checked. Figure 3 shows the “safe Tapping” advice for 1037 heats, with an overall performance of correct advices of 94.8%.
For the Green and Red area the performance is even better; with 924 out of 944 green/red correct advices a performance of 97.9% is accomplished.
For Phosphorous measurement, using Danieli Corus sublance measurement technology, a reliable tapping practice can be established without loss of production time or unnecessary de-qualifying of out-of-spec heats.