DIRECT MEASUREMENT OF NITROGEN IN LIQUID STEEL

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SUMMARY

This contribution concerns a newly developed system "Nitris®" for the fast and reliable in situ measurement of nitrogen in liquid steel. The partial pressures of nitrogen in liquid steel are high enough to be measured by a technique similar to the Hydris® technique. The major problem is the slow kinetics of the nitrogen exchange reaction between the liquid steel and the carrier gas.

A carrier gas is injected into the liquid steel and its nitrogen content is compared with that of the recollected carrier gas. The composition of the carrier gas is adjusted until the nitrogen content of the injected and the recollected gas are nearly equal and the equilibrium value can be calculated via a model.

Measurements have been performed in different steel grades. Results compare very well with analyses on samples in the laboratory (inert gas fusion or emission spectrometry). Reproducibility, accuracy and reliability of the Nitris® analyses are often even superior. The new technique is however much faster and in situ.

This offers substantial benefits during manufacture of nitrogen sensitive and renitrogenised steel grades. It also can help in controlling steel processes, e.g. shrouding between ladle and tundish.

1. INTRODUCTION

The structure and the mechanical properties of steel are strongly influenced by interstitially dissolved nitrogen and by nitrides and carbonitrides of microalloying metals. Thus a close control of the nitrogen content is highly desirable. During liquid steel processing the nitrogen content can change by alloying additions, gas bubbling, contact with air, vacuum treatment, etc.

It is now common practice in steel plants that samples taken from the liquid steel are analyzed for nitrogen with the carrier gas fusion technique, which has a good accuracy. Yet, for some applications this accuracy is not sufficiently high. Also, the overall accuracy of this measuring method can be severely reduced by errors introduced by the sampling procedure, including acquisition and preparation of the sample. Nitrogen can easily be picked up from contact with nitrogen containing parts of the sampler or even from contact with the surrounding air, and also in the laboratory during drilling, punching and cleaning of the sample nitrogen can be picked up or lost. In addition, the reference samples used for calibration can be a source of inaccuracy[1]. The major disadvantage of the classical analysis technique is certainly the long analysis time (5 minutes or more). This makes the technique less suitable for process control in steelmaking operations.

Heraeus Electro-Nite developed a fast on-line method for the nitrogen determination of steel melts. This novel technique known as NITRIS® is based on the in situ measurement of the nitrogen exchange between a well determined injected gas and the liquid steel. The NITRIS® system consists of a disposable immersion probe for the gas transfer towards and from the liquid steel, a lance and gas cable for the gas transportation between probe and pneumatic unit and a pneumatic unit with processor for the gas analysis and the system control. The components of the NITRIS® system are shown in figure 1.

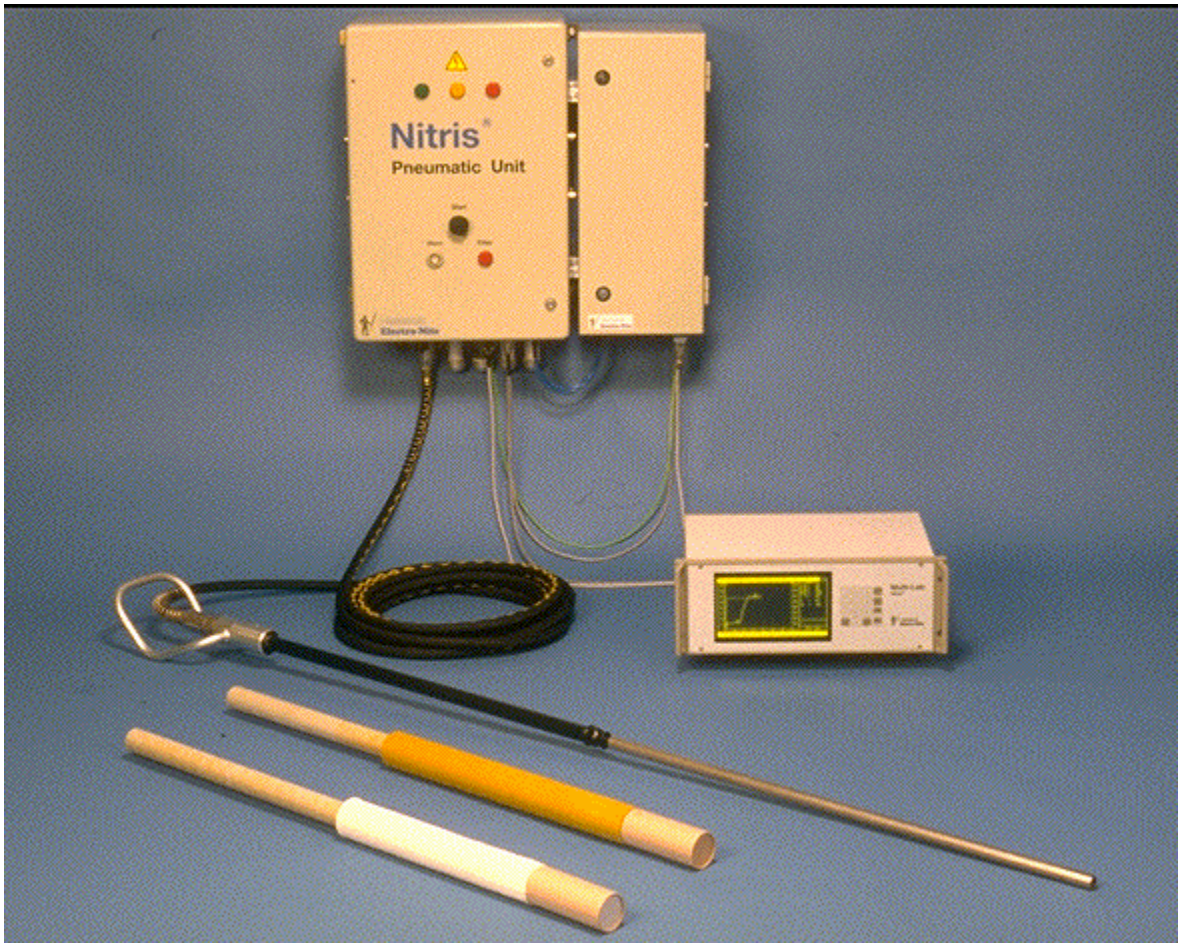

Figure 1: The NITRIS® system (showing: pneumatic unit, processor unit, pneumatic cable, lance and immersion probes)

2. THEORETICAL CONSIDERATIONS

Solubility of nitrogen in liquid steel.
The equilibrium between monatomically dissolved nitrogen in liquid steel and the gaseous nitrogen molecule is described by Sieverts' law:

$$f_N(N\%) = K_N(pN_2)^{-1/2}$$

where

f_N = activity coefficient for nitrogen in steel, departing from unity by varied influence of elements other than iron present in steel.
K_N = temperature dependent equilibrium constant of the dissolution reaction.
pN_2= partial pressure of nitrogen in carrier gas.

This relationship is used to calculate the weight per cent nitrogen in the liquid steel, N%.

Nitris® measuring principle.
The Nitris® measurement methodology is based on the nitrogen exchange between a gas, which is in contact with the liquid steel for a certain period of time. The complete theoretical description of the system can be found in Plessers et al [(2)] and Jungreithmeier et al [(3)].

Practically the measuring procedure is the following:
1. Pure helium gas in injected and the absorbed nitrogen is determined.
2. Based on the absorbed nitrogen a gas mixture to be injected is made.
3. After the injected gas mixture becomes stable, the recollected gas is measured. By using the law of Sieverts the nitrogen content in the steel can be calculated. To minimize errors, the exchange measurements are repeated until the injected nitrogen mixture has a composition in the neighbourhood of the equilibrium. Figure 2 shows a Nitris measurement trace in which the 3 consecutive steps can be recognised.

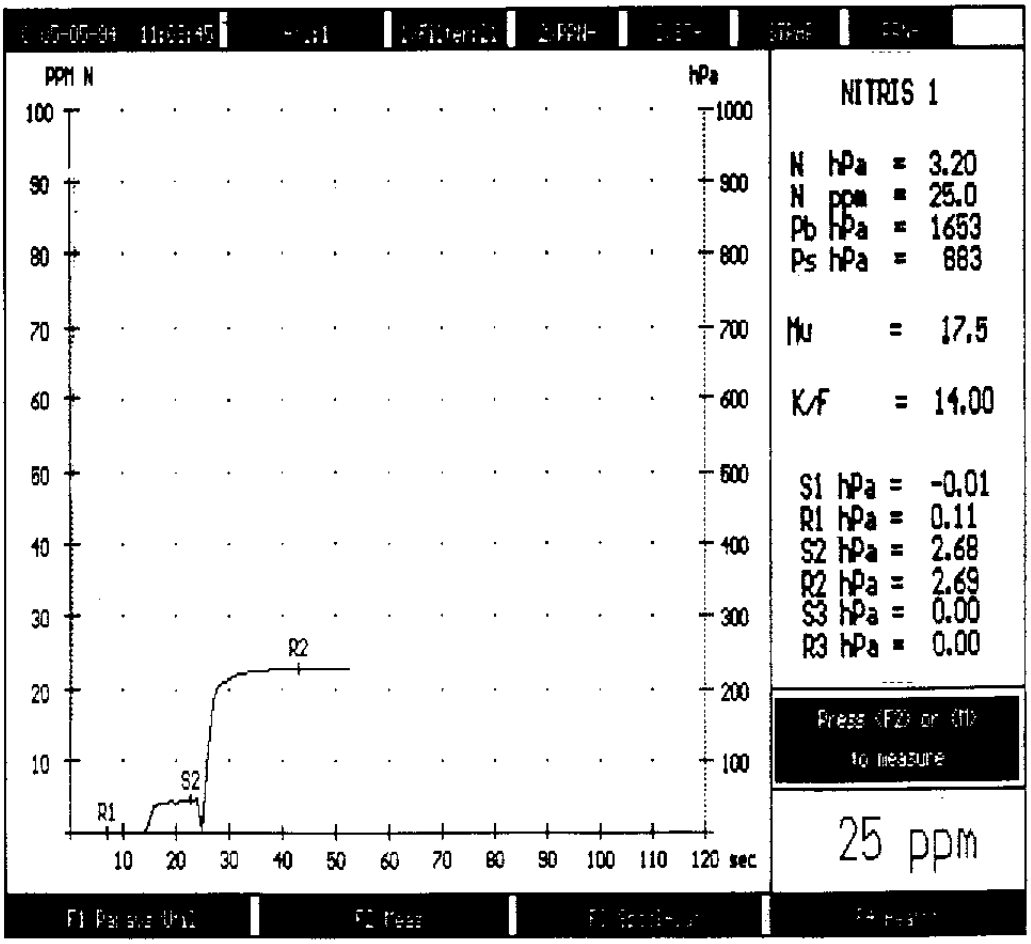

Figure 2: Typical Nitris® measurement trace

3. RESULTS

Comparison with conventional nitrogen analytical techniques.
The Nitris® system has been successfully demonstrated in various steel plant applications, including ladle, degasser and tundish. Figure 3 shows the comparison in these applications for 6 different steel plants with the conventional techniques. The points in the graph are in general the mean of two samples which where analyzed for nitrogen with inert gas fusion or spectrographic analysis.

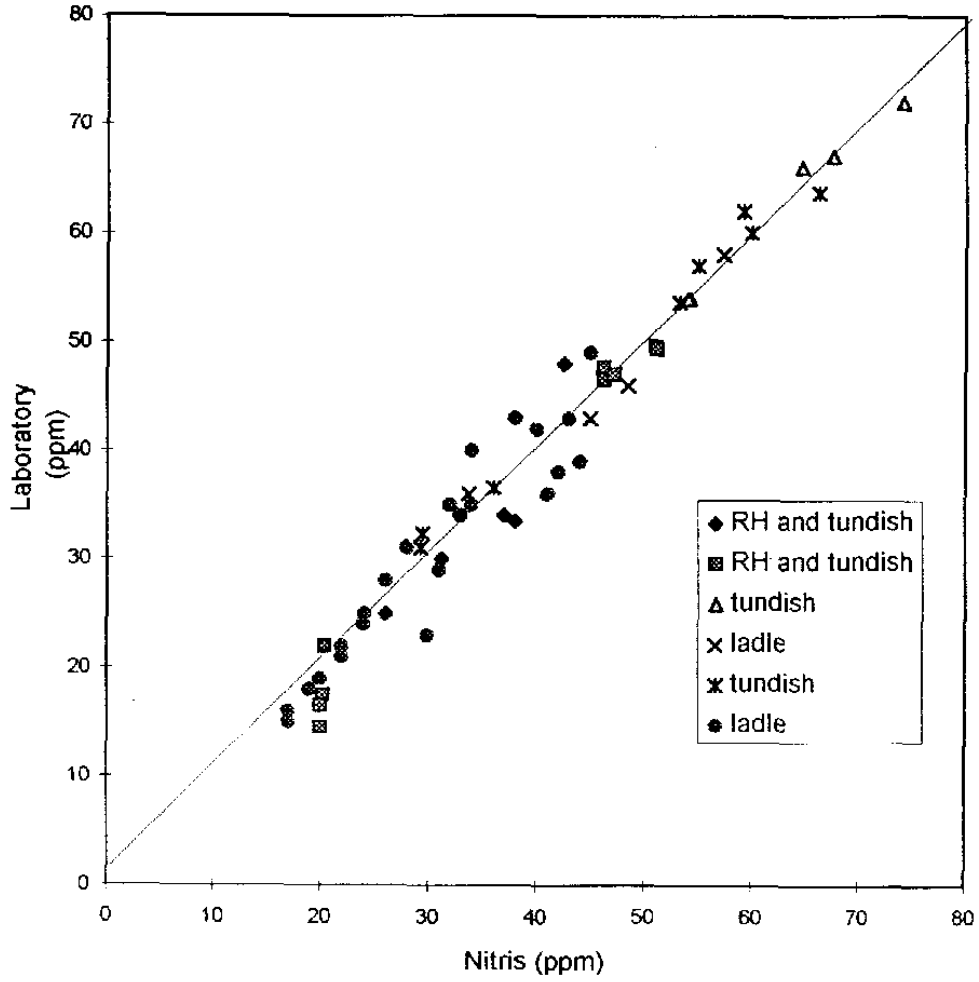

Figure 3: Comparison Nitris-Lab for different steelplants

It is seen that for these applications in the different steel plants a good correlation exists between the Nitris® results and the laboratory results. Also no difference between applications can be found. However, in a number of steelplants a systematic deviation between the two methods of analysis can be seen[3] In those cases the laboratory analyses were lower than the Nitris® measurement results (about 5 ppm).

In comparison with the existing methods for nitrogen analysis in solid steel, gas combustion analysis and optical emission spectroscopy, the Nitris® measurement system has a time advantage. The nitrogen result in ppm is displayed by the Nitris® measurement system in about 1 minute. The time for the conventional methods is composed of the sampling, sample transportation, sample preparation and the off-line analysis. This results in a significantly longer total analysis time and often requires about 10 minutes. Waiting for a nitrogen result in the steel shop control room is a common headache, disturbing

pre-set steel flow models. The overall accuracy of the analysis is also negatively influenced by the different steps by the conventional off-line methods as a strict control of each step is required to minimise the errors.

Precision of Nitris®

The precision of Nitris® has been demonstrated by repetitive analysis in ladle and tundish applications. These measurements showed that for nitrogen contents lower than 50 ppm all the measurements fall within ± 2 ppm of the calculated mean. Above 50 ppm this is around ± 4 to 5 %.

Figure 4 shows the nitrogen profiles measured in a tundish in which two steel grades with different nitrogen content are poured. The mixing of the steel grades can easily be followed. These measurements were performed with two different Nitris® systems. As can be seen an excellent agreement between the systems is found.

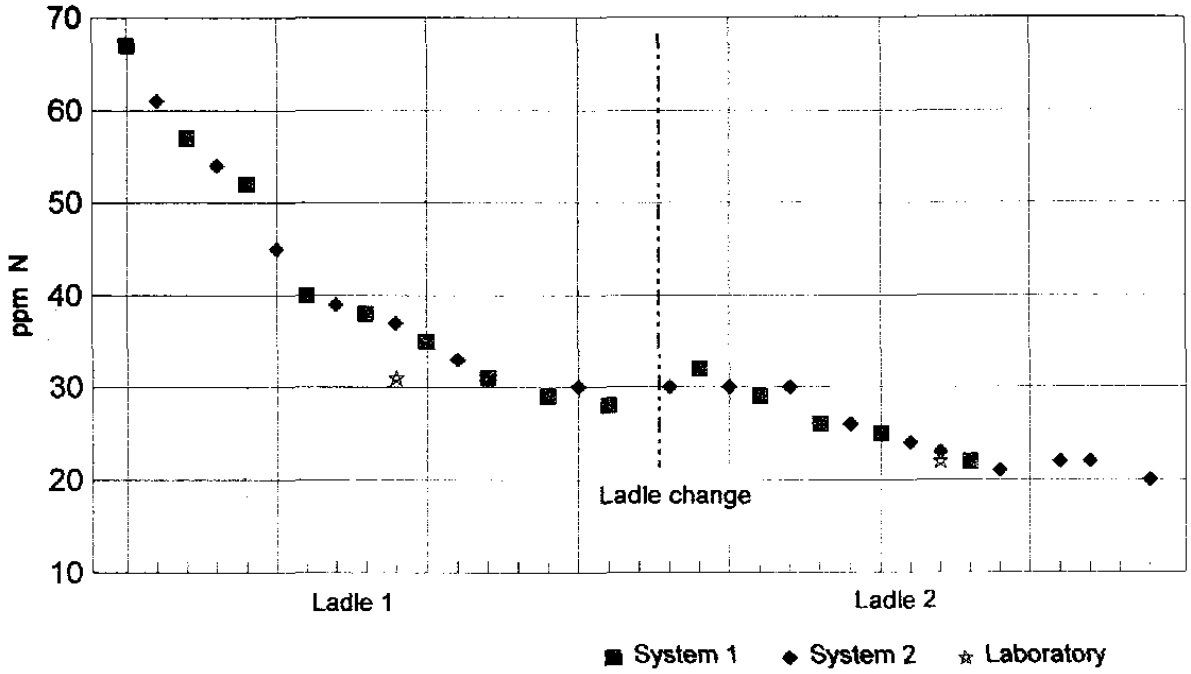

Figure 4: Tundish nitrogen profile as measured by two independent Nitris® systems

4. CONCLUSION

The Nitris® system allows a fast nitrogen determination with a high accuracy and precision. Therefore Nitris® offers a couple of practical advantages to the steelmaker:

- Immediate change-over of steel grade when the heat is out of the nitrogen specifications in secondary metallurgy. This results in minimised down grading of the final product.
- Precise adjustment of nitrogen according to the specifications for those grades with restricted nitrogen ranges. Controlled adjustments can be made after an on-line Nitris® measurement, with gains on accuracy and flexibility. The use of nitrogen purging gas will more frequently be possible due to a quick and accurate yield control. Gaseous nitrogen then replaces solid nitrogen carrying alloyers, which often suffer from poor yield due to slagging.

- Titanium and/or boron savings in Interstitial Free (IF) Ultra Low Carbon (ULC) grades. It is today common practise to extra charge these alloyers by as much as 20 % as a security margin to the upper nitrogen margin. Their addition downstream off aluminium kill and a Nitris® measurement enables precise direct addition.
- Leakage control of the sliding gate and shrouding system when concasting. Air(nitrogen) pick-up can rapidly be measured. This allows for actions around the pouring system to be taken.
- Follow up of nitrogen profiles in continuous sequence casting.
- Precise grading of as-cast products.

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To be published in: Scaninject VII, 7th International Conference on Refining Processes, June 7-8, Luleå, Sweden