Heraeus

Hydris® Application Guide

Electro-Nite

1 About Hydris

1.1 Hydris measurement principle

1.1.1 Configuration

The Hydrogen Direct Reading Immersion System (Hydris)[1] measures the hydrogen concentration in a specific gas mixture, and calculates the hydrogen content in liquid steel.

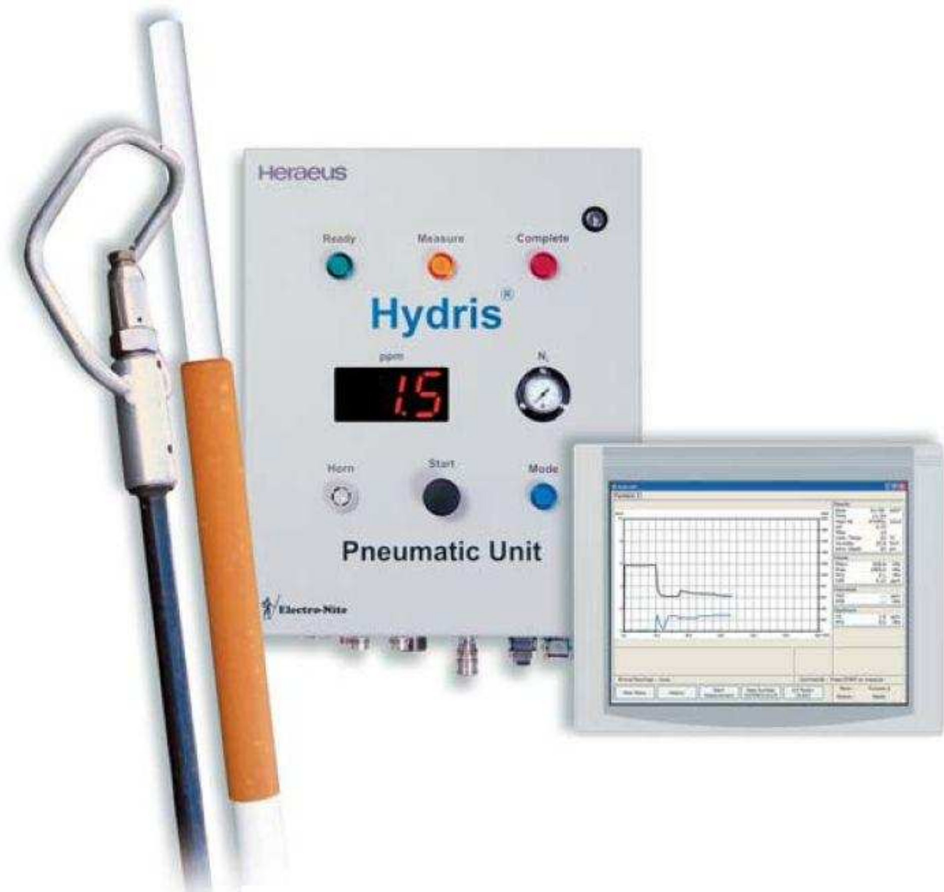

Figure 1: Hydris system

The basic components are:

- Processor unit that controls the pneumatic system and displays the hydrogen results
- Pneumatic unit
- Interface cable for communication between the processor unit and the pneumatic unit
- Pneumatic cable linking the pneumatic unit and the lance
- Lance for immersing the probe in the steel bath
- Disposable probe

1.1.2 Method

Nitrogen carrier gas is injected in the steel melt and recirculated between the melt and the pneumatic unit. It picks up hydrogen during its passage in the melt. The measurement is stopped when the equilibrium is reached between the hydrogen dissolved in the melt and hydrogen in the carrier gas:

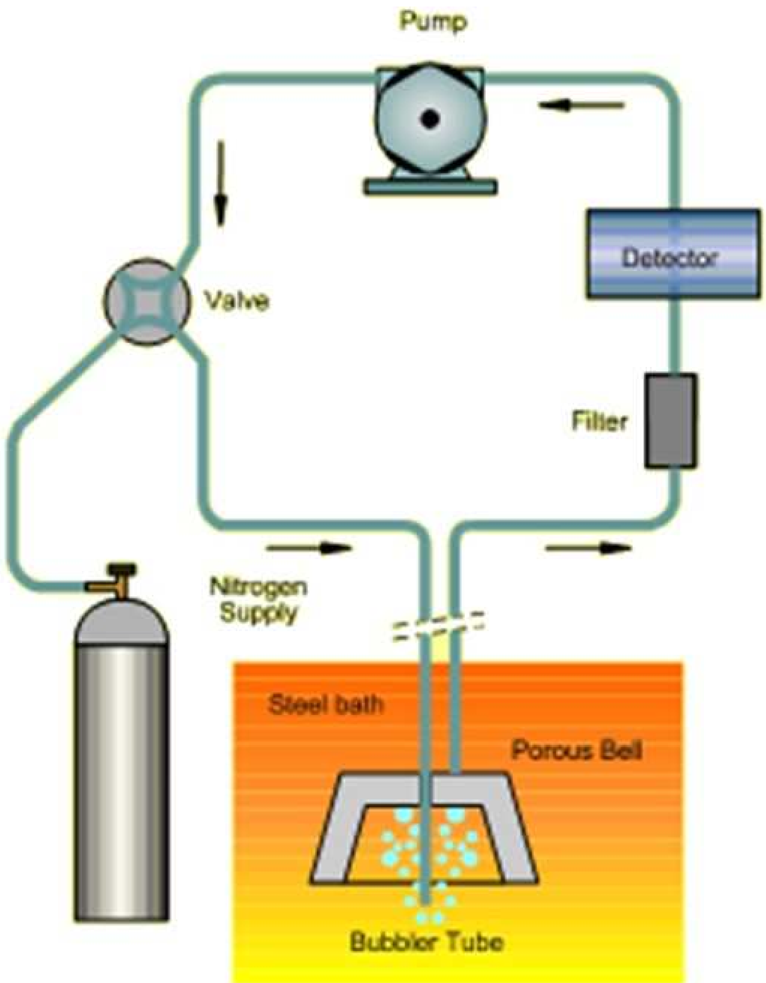

Figure 2: Measurement principle

The following figure shows an example of a Hydris hydrogen measurement:

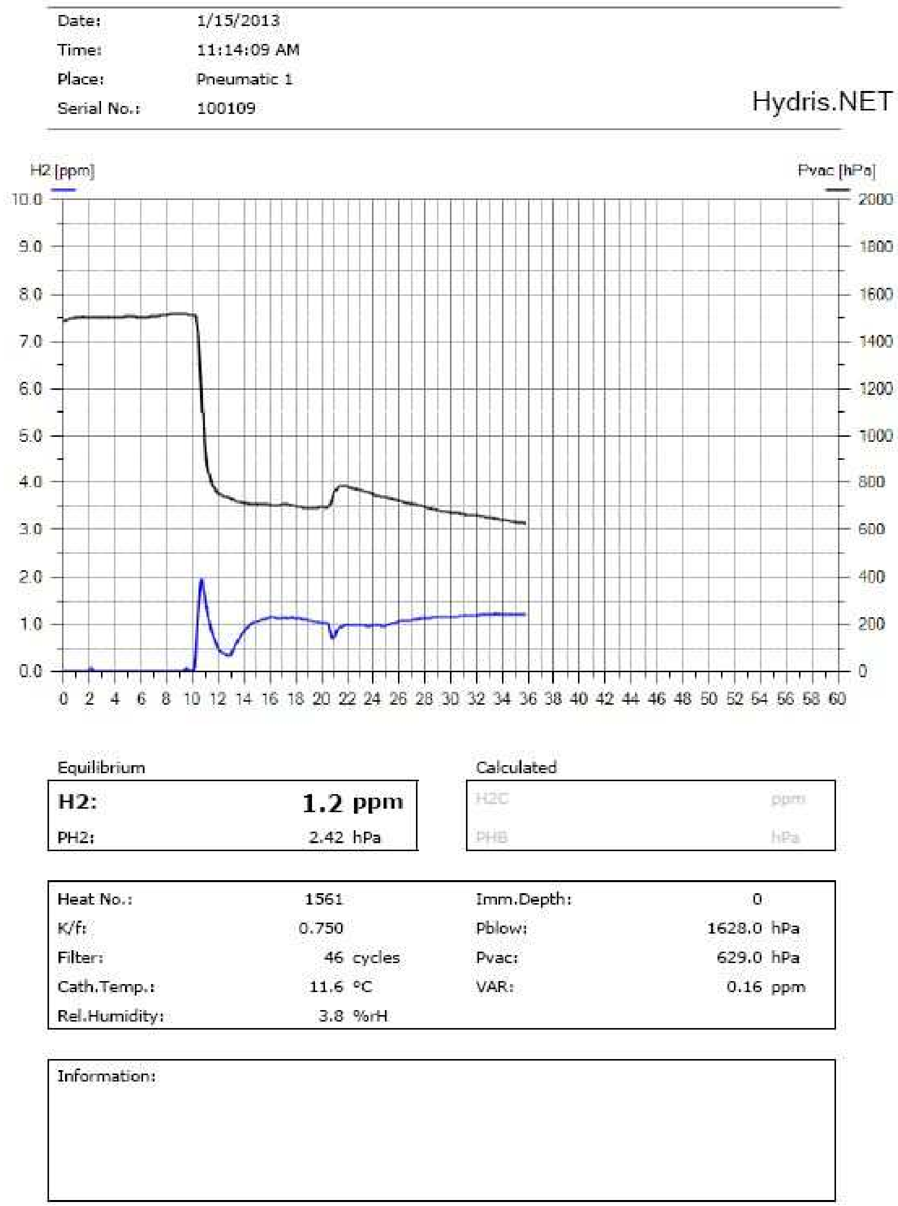

Figure 3: Example of a Hydris measurement showing hydrogen concentration

1.1.3 Analysis technique

The hydrogen content in the recirculated gas mixture is analysed using the thermal conductivity detector inside the pneumatic unit. Due to the enormous effect of hydrogen on thermal conductivity in gas mixtures, the hydrogen concentration can easily be measured. The hydrogen concentration is converted to the hydrogen content of the melt in accordance with Sieverts' law, which states that:

$$H = K / f * \sqrt{pH_2}$$

Where:	H	=	Hydrogen in ppm
	pH_2	=	Hydrogen partial pressure in hPa
	K	=	Equilibrium constant of the reaction
	f	=	Hydrogen activity coefficient

Figure 4 shows the thermal conductivity of different gases. As the difference in thermal conductivity between hydrogen and nitrogen is significant, even small amounts of hydrogen can easily be detected.

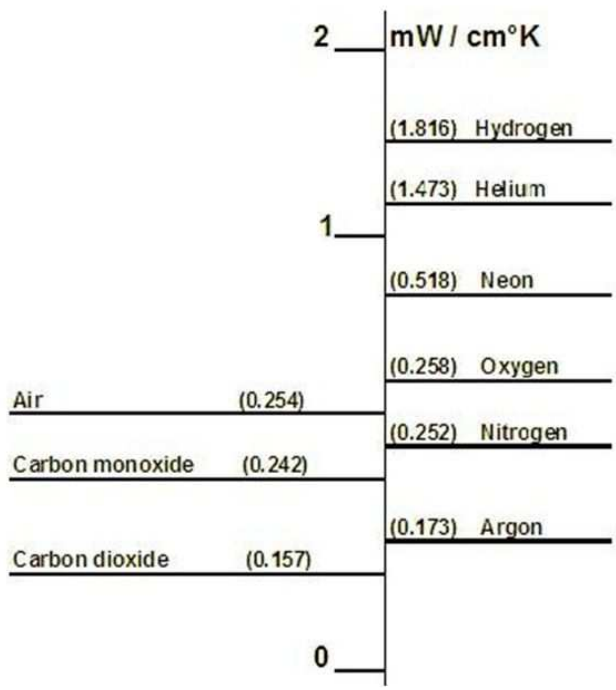

Figure 4: Thermal conductivity of gases

1.1.4 Hydrogen equilibrium detection

When Hydris was first introduced, some differences were found between existing hydrogen samplers and Hydris. Different experiments were set up to prove that Hydris correctly measured the hydrogen equilibrium content. These experiments were subject of a paper[2]. One typical experiment is described below.

Two different carrier gases were used to measure the hydrogen level in steel: The first gas contained no hydrogen at all (100% nitrogen). The second carrier gas, however, contained 15% of hydrogen and 85% of nitrogen, equivalent to a hydrogen equilibrium value in steel of 9.2ppm (K/f=0.75).

A hydrogen measurement using pure nitrogen as carrier gas is characterised by a continuous diffusion of hydrogen into the carrier gas, until equilibrium is reached between melt and gas. The carrier gas containing 85% nitrogen and 15% hydrogen is in excess of hydrogen and will, during its circulation through the melt, continuously lose its hydrogen to the steel until the hydrogen in the carrier gas and the hydrogen dissolved in steel are in equilibrium.

The hydrogen equilibrium value is independent of the hydrogen content in the carrier gas. Consecutive Hydris measurements using these two different carrier gases also showed identical hydrogen equilibrium values (see figure 5).

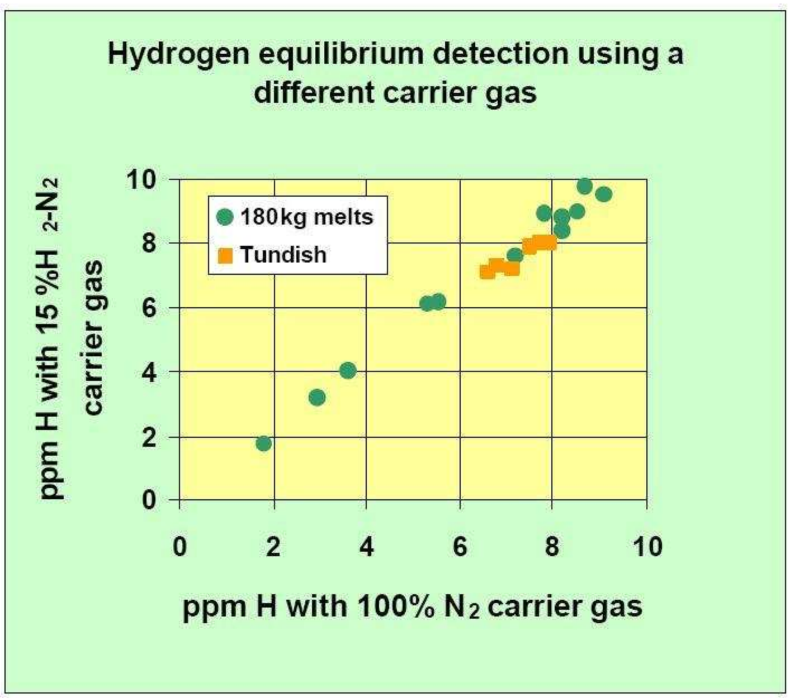

Figure 5: Detection of hydrogen equilibrium using two different carrier gases[2]

1.2 Hydris characteristics

1.2.1 Measurement limits

Hydris is able to measure all metallurgical hydrogen contents in liquid steel. The measurement time increases with higher hydrogen contents. A simple modification of parameters allows the Hydris user to optimise the measurement conditions.

1.2.2 Application limits

Problems can occur when the:

- Oxygen level exceeds 200ppm
- Titanium level exceeds 0.08%
- Sulphur level exceeds 0.2%
- Bath temperature exceeds 1680℃

1.2.3 Measurement accuracy

Hydris has proven to be a very accurate hydrogen analyser. Experience in different steel grades has shown that 95% of the measurements lie within a scatter range of ± 5% relative.

Possible drift of the thermal conductivity detector can be checked and recalibrated by the use of calibration gases.

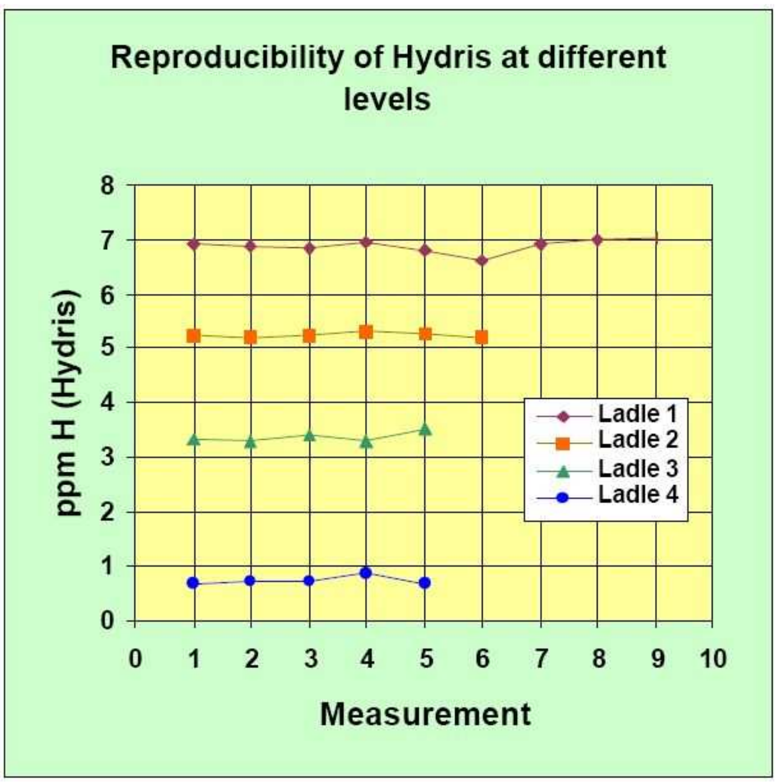

Figure 6: An example of the reproducibility of Hydris at different hydrogen levels

1.2.4 Low hydrogen range

The Hydris.NET measurement system covers the low hydrogen application range down to below 1ppm. The measurement accuracy required in this range is accomplished by:

- Pressure compensation
- △T compensation of the thermal conductivity detector
- Enhance zero adjustment
- Automatic immersion depth compensation

The maximum hydrogen value in steel grades has become increasingly lower over the years:

Application	Previous levels	Current levels
Rail steel	2 – 5 ppm	1.2 – 3.5 ppm
Heavy plate, lower sulphur	2 – 3.5 ppm	1.5 – 3.5 ppm
Forged ingots	1 – 3 ppm	0.5 – 2.5 ppm

Automatic immersion depth compensation:

The immersion depth slightly affects the hydrogen measurement. This is because the partial pressure of hydrogen as measured by the system is the result of the measurement of the hydrogen content in the carrier gas (analysed as %) in combination with the total pressure at the point of measurement.

Immersion depth compensation can be set to automatic or manual. The correction applied during immersion of the Hydris probe further optimises the determination of hydrogen.

1.2.5 QuiK-Read measurement

The Hydris measurement system uses the equilibrium method to determine the hydrogen content. Alternatively, when measuring in the range above 4ppm, there is a QuiK-Read method that determines the hydrogen content in approximately 30 seconds. This is achieved by calculating the final content based on the measurement taken at an earlier phase. The result is comparable in accuracy to those obtained using the equilibrium method. Short measurement times in the medium to high ppm range allow:

- Quick determination of hydrogen content
- Reduced thermal load on the immersion lance
- Reduced load on the pneumatic system

1.2.6 Computer interfaces

The basic Hydris.NET unit is delivered with some standard interfaces and some optional ones.

Standard interfaces are:

- TTY 20mA
- Ethernet
- USB

Optional interfaces are:

- Profibus DP
- Modbus RTU
- Data access using OPC

1.2.7 Multiple station installation

One Hydris.NET processor can operate with one or two pneumatic units serving one measurement station each. Each measurement station has its own parameter data to ensure optimum adjustment to the measurement requirements. The processor is connected to the pneumatic units using the Ethernet network.

1.2.8 .NET application

Hydris.NET operates as part of the plant network using the Ethernet communication interface. Hydris.NET can be used to:

- Maintain the Hydris database.
- Configure Level2 input and output telegrams, which includes creating the content, specifying the target and destination, and 'binding' IO types to measurement places.
- Configure OPC communication, which includes specifying how Hydris components communicate with external components through OPC. OPC is Object linking and Embedding for Process Control: a software interface standard that allows Windows programs to communicate with industrial hardware devices.

1.3 Hydrogen sampling techniques

Various techniques have been used in the past, with varying degrees of success, to obtain a good hydrogen sample.

Open quenched sampling methods quench a pin as quickly as possible in water and then liquid nitrogen in order to "freeze" the hydrogen in the sample. Manual handling can easily introduce errors.

One such open quenched method uses an evacuated pin tube. This tube is immersed directly in the steel. The quartz tube opens and steel is sucked into the quartz tube. The recovery of the sample requires manual handling, which can introduce errors. This method provides a quick filling, however premature opening of the sample results in poor hydrogen readings.

A comparison between these different open quenched sampling methods shows that when using different techniques, different hydrogen results are obtained. The experience of the operators taking the samples is the most influencing factor.

1.3.1 Analysing non-degassed melts

Even if hydrogen sampling is a standard practice, diffusion of hydrogen from the sample to the air cannot always be avoided, resulting in hydrogen values that are too low.

Figure 7 shows examples of analyses of two different labs giving hydrogen values that are too low. In Lab 1, the difference between the lab and Hydris increases as soon as hydrogen (by Hydris) exceeds levels of more than 4ppm. In Lab 2, all hydrogen has diffused before being analysed because of poor sample manipulation:

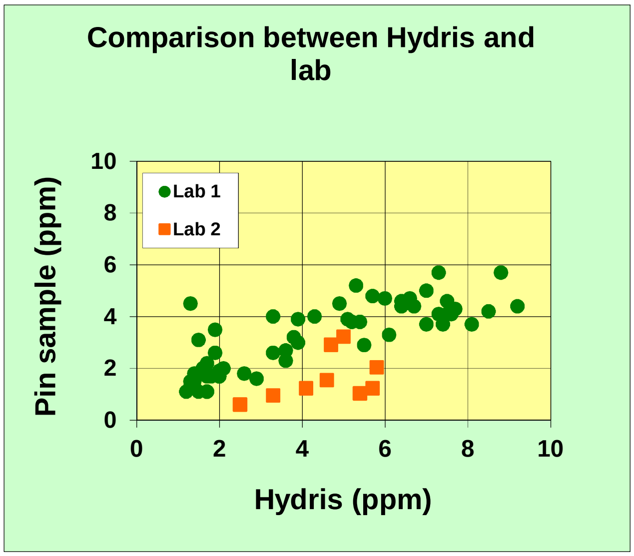

Figure 7: Analysing the same sample in different labs gives different results.

1.3.2 Analysing degassed melts

When low hydrogen values are to be analysed, the lab tends to give slightly higher values. This is explained by a small pickup when sampling in a spoon, but also due to the occurrence of piped samples and slag entrapment.

For very low values (<1ppm), the evolution of traces of C and N_2 from the graphite crucible and pedestal and the N_2 carrier gas can lead to the formation of cyanide, which interferes with the thermal conductivity cell of the hydrogen analysers[6].

1.4 Hydris probes

Hydris probes can be used to take hydrogen measurements in the:

- Ladle: to check initially and after degassing treatment
- Tundish: to prevent hydrogen-induced:
  - Breakouts, for example, in thin slabs and stainless grades
  - Cracks, for example, in rails and heavy plates
- Ingot casting: to prevent flakes in forgings

1.4.1 Probes for low-alloyed, aluminium-killed steel

For the ladle:

- 500mm and 900mm with non-splash refractory sleeve
- 750mm and 900mm with non-splash refractory sleeve for autolance

For the tundish:

- 380mm and 500mm with low thermal mass, non-splash refractory sleeve
- 380mm and 900mm with low thermal mass, non-splash refractory sleeve

For ingot casting:

- 380mm and 500mm with low thermal mass, non-splash refractory sleeve (aluminium cap without cardboard)
- 380mm and 900mm with low thermal mass, non-splash refractory sleeve (aluminium cap without cardboard)

1.4.2 Probes for Mn/Si semi-killed and free-cutting steel with S > 0.200%

For the ladle:

- 500mm and 900mm with non-splash refractory sleeve
- 750mm and 900mm with non-splash refractory sleeve for autolance

For the tundish:

- 380mm and 500mm with low thermal mass, non-splash refractory sleeve
- 380mm and 900mm with low thermal mass, non-splash refractory sleeve

1.4.3 Probes for high-alloyed and stainless steel

For the ladle:

- 500mm and 900mm with non-splash refractory sleeve
- 750mm and 900mm with non-splash refractory sleeve for autolance

For the tundish:

- 380mm and 500mm with low thermal mass, non-splash refractory sleeve
- 380mm and 900mm with low thermal mass, non-splash refractory sleeve

For ingot casting:

- 380mm and 500mm with low thermal mass, non-splash refractory sleeve (aluminium cap without cardboard)
- 380mm and 900mm with low thermal mass, non-splash refractory sleeve (aluminium cap without cardboard)

See the Hydris.NET sales brochure or your Heraeus Electro-Nite representative for order numbers.

2 Hydris applications

2.1 Primary steelmaking

2.1.1 Electric arc furnace

Normal practice does not allow the Hydris user to take measurements in the electric arc furnace due to the high oxygen levels.

Influence of the process on the hydrogen level:
The hydrogen levels obtained at the end of the process in an electric arc furnace are on average between 2 to 4ppm and higher in comparison to top blowing converters. The following factors determine the final hydrogen content:

- The use of lime - very sensitive for hygroscopic capacities
- The amount of charge carbon and oxygen blowing. The hydrogen level automatically decreases during oxygen blowing. Initially, hydrogen pickup takes place due to the stirring of the small steel bath. After oxygen blowing, a drop in hydrogen is observed due to the burning of the carbon.
- Slag capacity - the use of lime-aluminium slag results in a higher water capacity of the slag
- Scrap
- Leaking of cooling water from the electrodes
- Atmospheric conditions

2.1.2 Converter

Normal practice does not allow the Hydris user to take measurements in the converter due to the high oxygen levels.

Influence of the blowing processes on the hydrogen level:

Top blowing processes:
Hydrogen levels at the end of blowing should be between 1 and 2ppm. Burning through of the oxygen lances can, however, result in a serious hydrogen pickup.

Bottom blowing processes:
When bottom blowing processes are used, the oxygen is blown through the bottom. To avoid excessive heat near the blowing tuyere, some hydrocarbon cooling gases are used, resulting in the formation of hydrogen.

The concentration of hydrogen in the metal is determined by the intensity of two processes occurring in parallel: The dissolution of gases and the removal of gases from the metal together with CO bubbles. When the heat finishes in a very low carbon content, the concentration of CO in exhaust gases becomes very low and the partial pressure of H_2/H_2O gradually increases. Blowing with inert gases before tapping should, however, reduce the hydrogen content.

Steel makers should also consider the hydrogen pickup phenomena when tapping the steel into a ladle. Using preheated ladles, the use of lime or other additions could result in high hydrogen levels in the ladle, even before ladle treatment.

2.3 Ladle metallurgy

Measuring conditions:
When taking a Hydris measurement in a ladle stirring station:

- The measurement should not be taken during argon or nitrogen stirring. Pickup of these gases will disturb the Hydris reading. Optimal measurements can be obtained when the operator waits one minute after the end of stirring, to enable small slag particles to float to the surface instead of adhering to the porous stone during measurement.
- If a hard slag is to be expected, it is advisable to break the slag by using a sampler before the Hydris measurement is taken.
- Measurements are taken as vertically as possible

When taking a Hydris measurement in a ladle furnace:

- Avoid excessive heating of the lance during measurement. The lance design and use of telescopic cardboard tubes protects the lance.

Influence of the ladle stirring/ladle furnace process on the hydrogen level:
The hydrogen level rises during the ladle stirring/ladle furnace process due to:

- The use of lime (or other slag formers) to reduce the sulphur content in the ladle can result in a large pickup of hydrogen
- Bad storage conditions of scrap or the use of rusty scrap results in an increase of hydrogen (see figure 8)

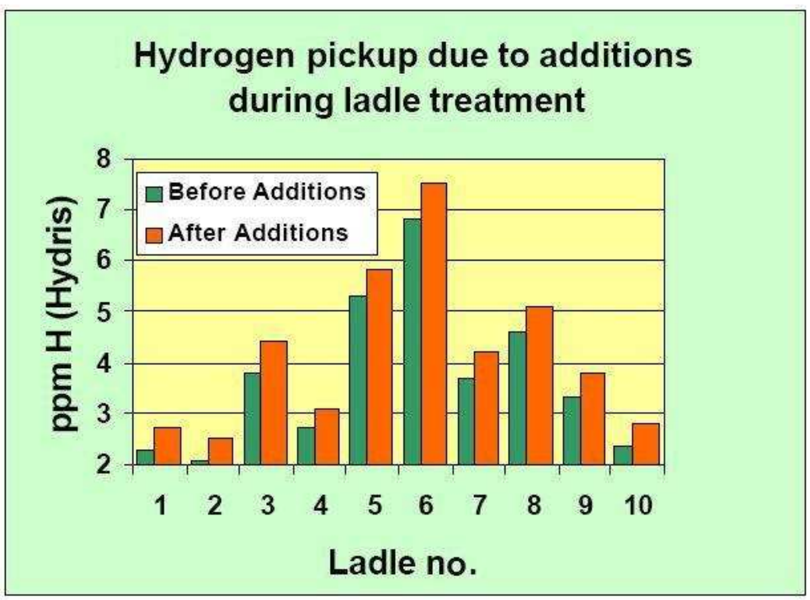

Figure 8: Hydrogen pickup during ladle treatment in a stirring station. Additions consist of scrap, aluminium wire, and ferroalloys

- The use of ferroalloys affects the hydrogen content.
- Aluminium and CaSi-wire only results in a very small hydrogen pickup (maximum 0.1ppm).
- Heating of the ladle results in a small hydrogen pickup, especially if the heating remains moderate.

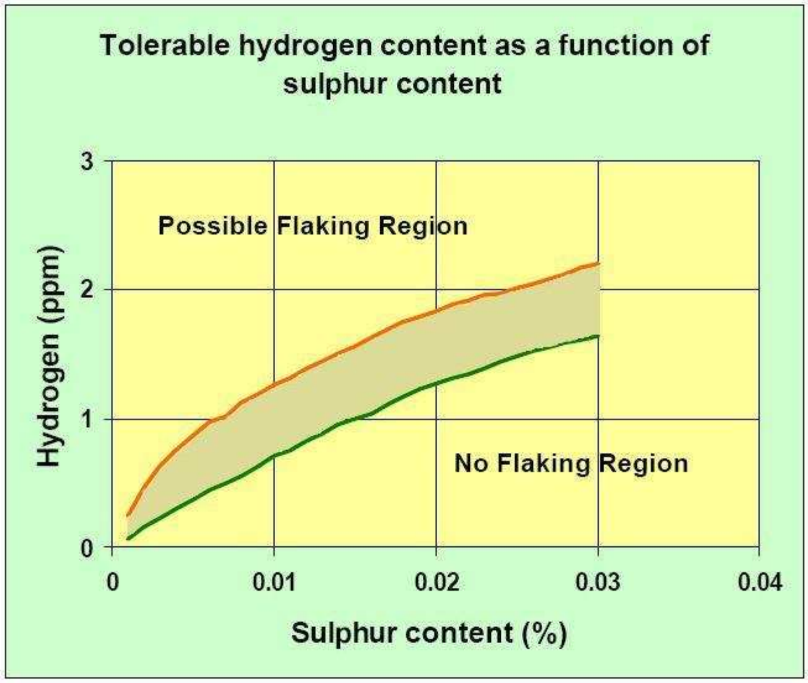

Figure 9: An example, found in literature ([8]), of a diagram illustrating the optimisation of the hydrogen/sulphur ratio to avoid flaking

Note: The Hydris measurement conditions can be optimised by using specific hardware for automatic lances (including a quickly replaceable probeholder and connection parts). They combine an optimal measurement technique with easy maintenance.

2.4 Degassing processes

Hydris provides the standard hydrogen level measurement before and/or after ladle treatment, typically at the degasser. The steel maker can decide to degas the steel heat if the hydrogen level is too high initially, and after the treatment to check that the targeted hydrogen level is sufficiently low. Additionally, these two measurements indicate the efficiency of the degasser unit and advices on potential maintenance of the steam ejectors.

- Accurate hydrogen measurements before and after degassing enable the process to be understood and optimised. The potential exists to reduce both the treatment cost and the final hydrogen concentration.

- Immediate hydrogen measurement at the end of the degassing cycle provides the steel maker with an improved quality monitor prior to sending the ladle to the caster or ingot station. The degassing unit is responsible for this procedure.

Measuring conditions:
The general guidelines for Hydris remain valid for all degassing applications:

- Try to dip as vertically as possible
- Hard slag must be broken before measuring

A distinction should be made between different degassing processes:

- **RH**: The specific circumstances of the RH process allow Hydris users to take hydrogen measurements during degassing. Try to avoid measurements near the down snorkel.

- **DH, VD, and VAD**: Due to the movement of the bath level (DH) during the process or the complete sealing of the ladle in tank degassers (VAD), it is impossible to take a Hydris measurement during degassing. The hydrogen measurement can only be taken before and at the end of the treatment. If a hard slag is to be expected, it is advisable to break the slag by using a sampler before the Hydris measurement is taken.

Influence of the degassing parameters on the final hydrogen content:

Vacuum pressure
A well maintained degassing unit is crucial in achieving very low hydrogen levels. Final hydrogen contents below 1ppm can only be achieved with vacuum pressures below 1mbar.

Initial hydrogen level
If only short degassing treatments are applied, it is essential to avoid initial hydrogen levels that are too high. Valuable time will be lost in eliminating the superfluous hydrogen. The initial hydrogen level is, however, less critical if longer degassing times are applied.

The use of additions
Additions of ferroalloys, lime, and so on at the end of the degassing treatment might spoil the degassing efforts as they can raise the hydrogen level due to hydrogen pickup.

The steel grade type
Some steel grades require longer degassing times to achieve very low hydrogen levels. Degassing of stainless steel grades result in hydrogen levels around 1.4ppm, whereas low alloyed grades easily come down to 0.7ppm.

2.5 Continuous casting

Measuring conditions:
When taking a Hydris measurement in the tundish:

- Ensure the Hydris probe is as vertical as possible. This can be done by optimising the design of the lance and the use of the smaller Hydris probe designed for the tundish.
- Avoid excessive leakage of the argon shielding gases around the ladle shroud.

Influence of continuous casting on the final hydrogen concentration:

<u>Hydrogen pickup in the tundish</u>
A pickup of hydrogen in the tundish is a natural phenomenon. At the start of a new sequence, special care must be taken to reduce the hydrogen pickup as much as possible. Despite the preheating of the tundish before the start of casting, the moisture deep in the lining slowly releases hydrogen that is gradually picked up by the steel. Figure 10 shows a typical example that shows the linear decrease of the hydrogen concentration in the tundish.

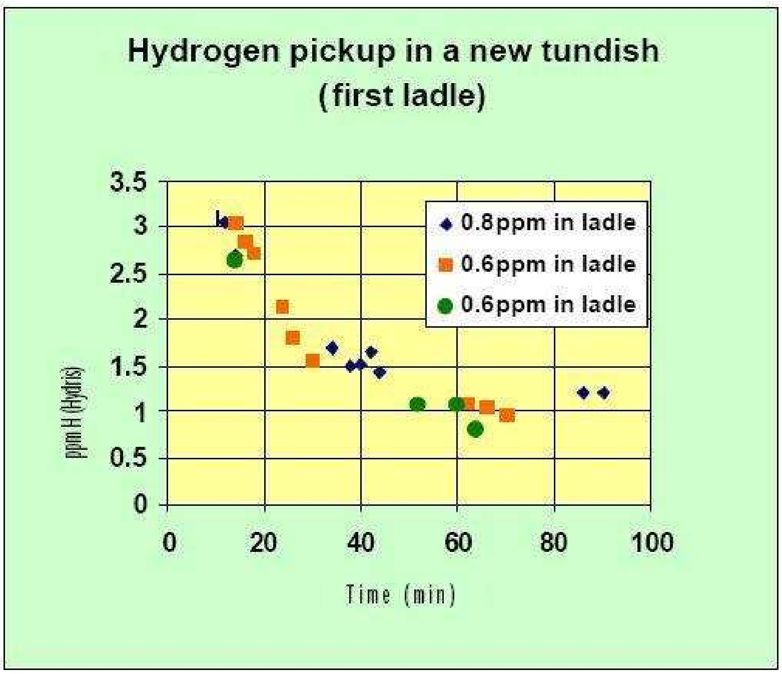

Figure 10: Linear decrease of the hydrogen content in a new tundish

The accuracy of Hydris allows very specific data to be obtained showing hydrogen pickup in the tundish. Figure 11 shows that for a particular tundish, the hydrogen level slowly increases to a maximum (for example, 15 minutes after the opening of the ladle), and decreases linearly to obtain a stable value after 30 minutes.

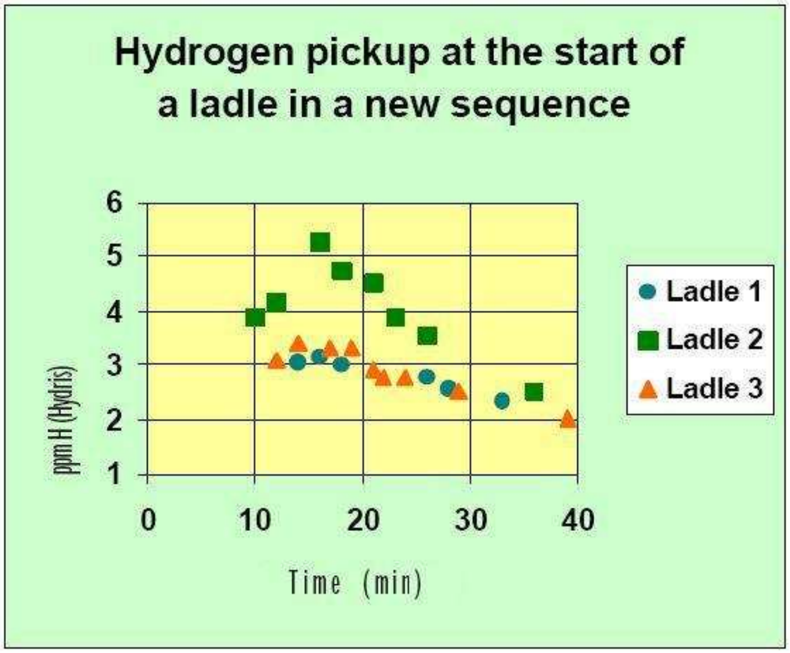

Figure 11: Detailed description of the hydrogen pickup with Hydris

From the second ladle onwards, an average pickup can be expected of around 0.3ppm under normal conditions. The hydrogen level of the previous ladle must be taken into account (figure 12).

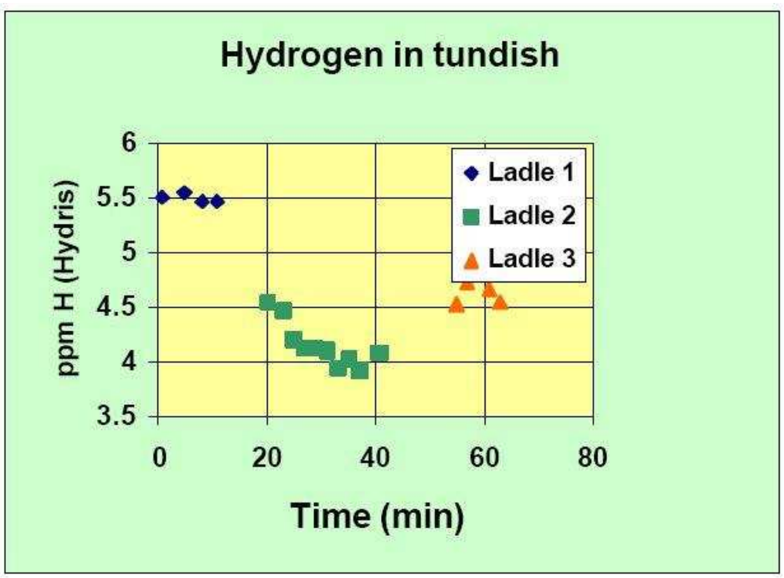

Figure 12: The ladle change occurred after 15 minutes. However, it took about 15 minutes of casting before the hydrogen level of ladle 2 was found. Total casting time of a ladle is 35 minutes

However, if the tundish runs empty during a ladle change, this could result in a small hydrogen pickup at the start of the new ladle. The hydrogen pickup remains moderate in a large tundish, but can become important in a very small tundish. Depending on casting speed and tonnage of tundish, this could take some time (figure 13). The pickup in a large tundish will be much smaller.

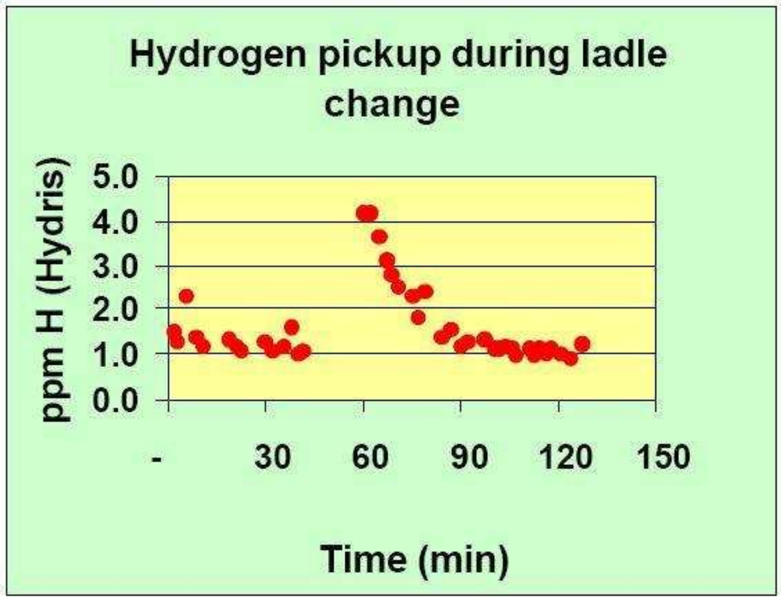

Figure 13: Hydrogen pickup during ladle change in a small tundish (6 tonnes)

Breakout detection

Various writers have confirmed a relationship between the hydrogen content in the steel and breakouts on the continuous caster[11]. Related breakouts are of the sticking type and are explained by the absorption of hydrogen into the mould lubricant. The gas bubbles cause crystallisation of the flux and increase in viscosity. As lubrication deteriorates, the tendency to breakouts increases. The risk of breakouts becomes very critical as soon as the hydrogen level exceeds 9ppm. These types of failures cannot easily be detected by pin samples as their reliability drastically decreases for high hydrogen levels.

Thin slab casting

The final product of the thin slab casters is also affected by the hydrogen content in the tundish. Excessive hydrogen content results in a deterioration of the cast quality and should therefore be monitored.

Hydris in the tundish:

Measuring with Hydris in the tundish means that the as-cast steel meets the internal or customised hydrogen specification. The internal specification mostly means making sure that the as-cast product is free from hydrogen-induced inner blowholes, cracks, surface defects, and mould break-outs. The customised hydrogen specification is meant to avoid flake formation in thick material like alloyed forging ingots, rails, beams, and automotive safety parts like axles and brake parts. Blowholes in solid steel indicate a high gas content coming from the sum of carbon monoxide, nitrogen, and hydrogen in which hydrogen has a far more significant influence than the other two. In stainless steel grades hydrogen above 10ppm sticker breakouts are caused by hydrogen diffusing into the lubricating crystallised mould powder layer.

Hydris and quality control

Hydrogen pickup in the tundish cannot be avoided. However, the accuracy of Hydris allows the steel maker to minimise hydrogen pickup by optimising tundish practice.
The accuracy of Hydris ensures that the steel maker can confirm the required quality standards. This confirmation is independent of the handling practices of the operators.
The accuracy of Hydris means that work schedules can be tightened and unnecessary thermal treatments avoided, thus saving money and simplifying production processes.

Hydris and breakouts
A direct hydrogen determination at the start of casting immediately informs the steel maker of the risk of eventual breakout. A decision can be made to either continue casting or to stop the casting sequence.

Hydris and thin slab casting
A direct hydrogen determination informs the steel maker of the casting conditions affecting final quality.

Hydris and direct rolling
Hydris is an essential tool for the rolling process. Directly rolled steel is more sensitive to flake formation, as cooling time is short after casting, decreasing hydrogen removal during cooling as the cast product. A direct hydrogen measurement is essential to determine the requirement for additional annealing treatments.

2.6 Ingot casting

Measuring conditions:
When taking a Hydris measurement in ingot casting:

- Increase the flushing times during measurement up to as much as 20 seconds due to the low superheat.
- Take the measurement as late as possible to obtain homogeneous conditions. However, take note of the temperature loss during casting.

Hydris in ingot casting:
Large forging ingots over 10 tonnes are checked for hydrogen directly in the mould when steel level has reached a suitable surface height for sensor immersion. If pouring or casting conditions prevent a direct in-mould measurement, the check has to happen in the ladle prior to casting. Depending on chemical composition and ingot size, alloyed forging ingots risk flake formation from hydrogen if the critical hydrogen level is exceeded. Flakes are internal structural cracks within the grain boundary layers caused by ionic hydrogen diffusion and reaction to molecular hydrogen with increasing volume.

Hydris and process control
Hydrogen pickup in the ingot cannot be avoided. The accuracy of Hydris allows, however, the steel maker to minimise hydrogen pickup by optimising the ingot casting practice.

The accuracy of Hydris ensures that the steel maker can confirm the required quality standards. This confirmation is independent of the handling practices of the operators. The measured hydrogen levels can determine the annealing process to be applied after casting.

3 References

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4 Figures