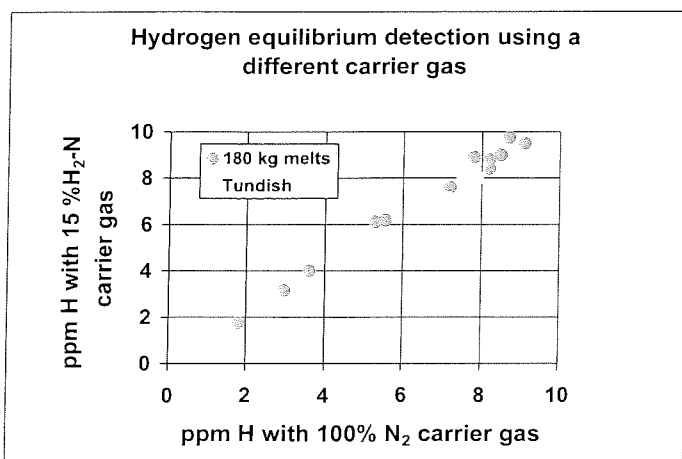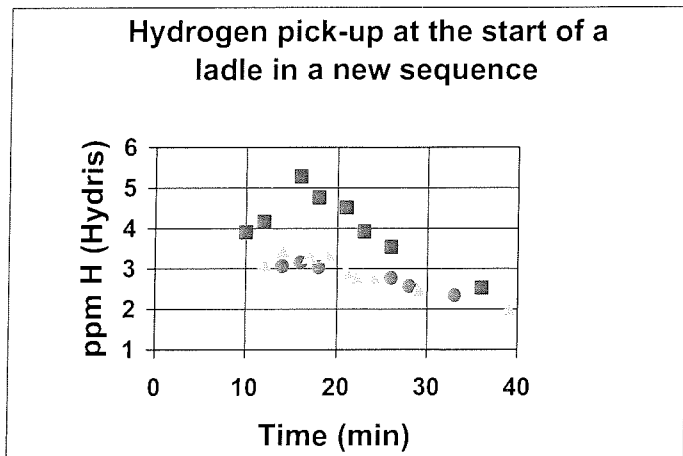# HYDRIS® APPLICATIONS
IN MODERN STEEL MAKING

- about Hydris®

- Hydris® applications in modern steel making

- Hydrogen in steel

Hydrogen pick-up at the start of a ladle in a new sequence

Hydrogen equilibrium detection using a different carrier gas

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Contents

Figure 1: The Hydris® system

I. ABOUT HYDRIS®

1 Hydris® Measurement Principle

A. Configuration

The Hydris® system[1] (figure 1) measures the hydrogen content in a specific gas mixture. Its basic components are:

   a. Processor unit that controls the pneumatic system and displays the hydrogen results
   b. Pneumatic unit
   c. Interface cable for communication between multi-lab Hydris® and pneumatic unit
   d. Pneumatic cable as a link between pneumatic unit and lance
   e. Lance for immersing the probe in the steel bath
   f. Disposable probe
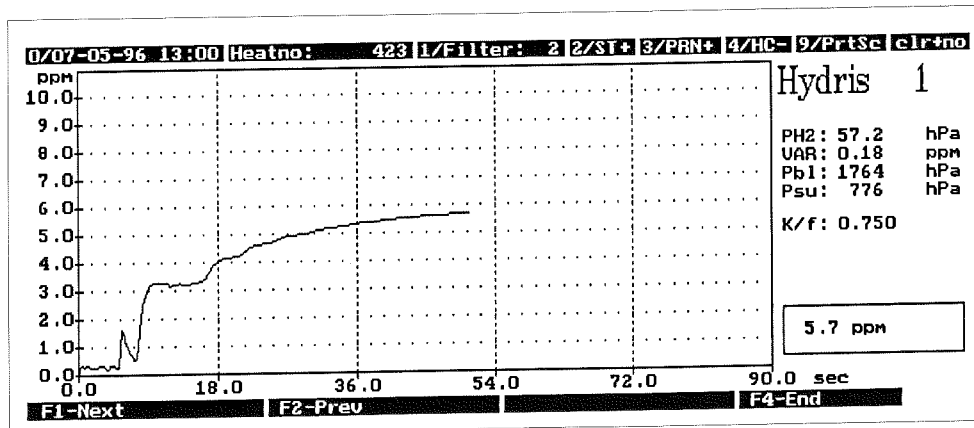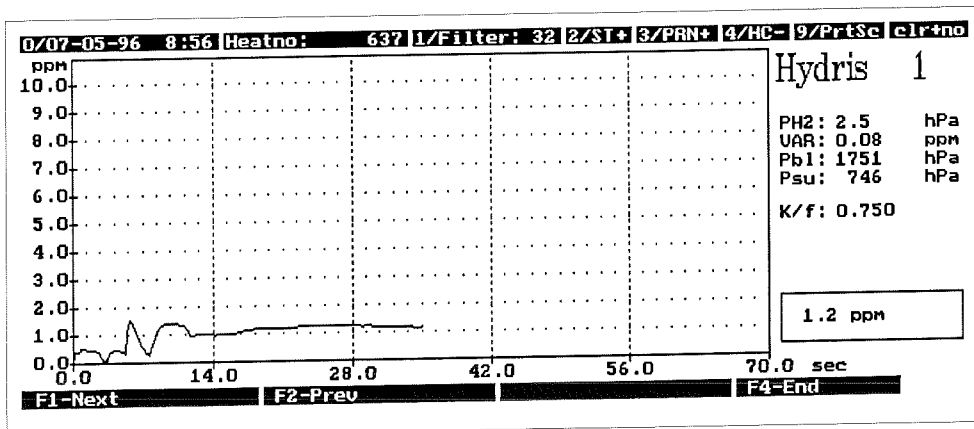
Figure 2: typical Hydris® measurements

B. Method

A nitrogen carrier gas is injected in the steel melt and recirculated between the melt and the pneumatic unit. It will pick 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 3). Examples of a few hydrogen measurements are shown in figure 2.

C. Analysing technique

The Hydris® system measures the hydrogen content by means of a thermal conductivity detector. It analyses the hydrogen concentration in the nitrogen carrier gas.

$$[H] = K/f \sqrt{P(H_2)}$$

with
$[H]$	=	Hydrogen content in steel (ppm)
$P(H_2)$	=	Partial pressure of hydrogen in the melt (hPa)
$Log\ K$	=	-1900/T + 1,9 (T in K)
f_H	=	Hydrogen interaction coefficient

Figure 4 shows the thermal conductivity of different gasses. As the difference in thermal conductivity between hydrogen and nitrogen is very significative, even small amounts of hydrogen can easily be detected.
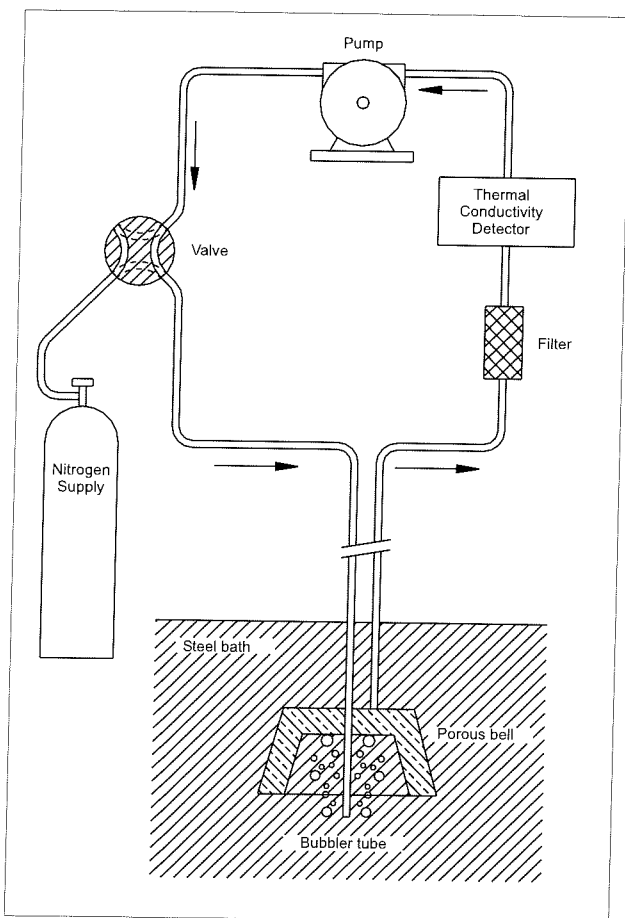
Figure 3: measurement principle
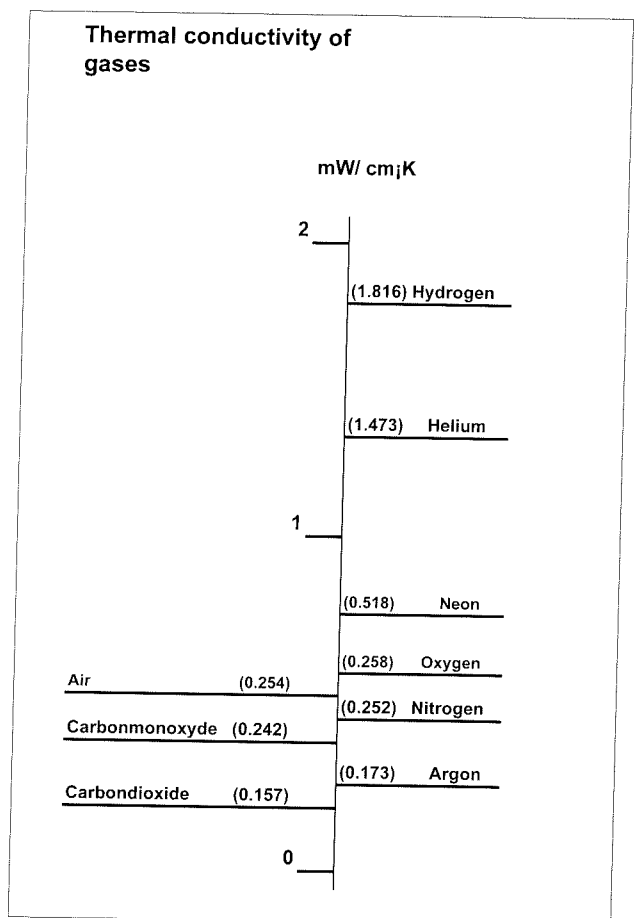
Figure 4: thermal conductivity of gases

D. Hydrogen equilibrium detection

At the introduction of Hydris®, some differences were found between existing hydrogen samplers and Hydris®. Different experiments were set up to prove that Hydris® measures correctly 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 did not contain any hydrogen at all (100% nitrogen). The second carrier gas, however, contained already 15 % of hydrogen and 85 % of nitrogen, equivalent to a hydrogen equilibrium value in steel of 9.2 ppm (K/f=0,75).

A measurement of hydrogen 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 show identical hydrogen equilibrium values (Figure 5). Hence, the hydrogen value as displayed by the Hydris® system represents the hydrogen content of the steel.
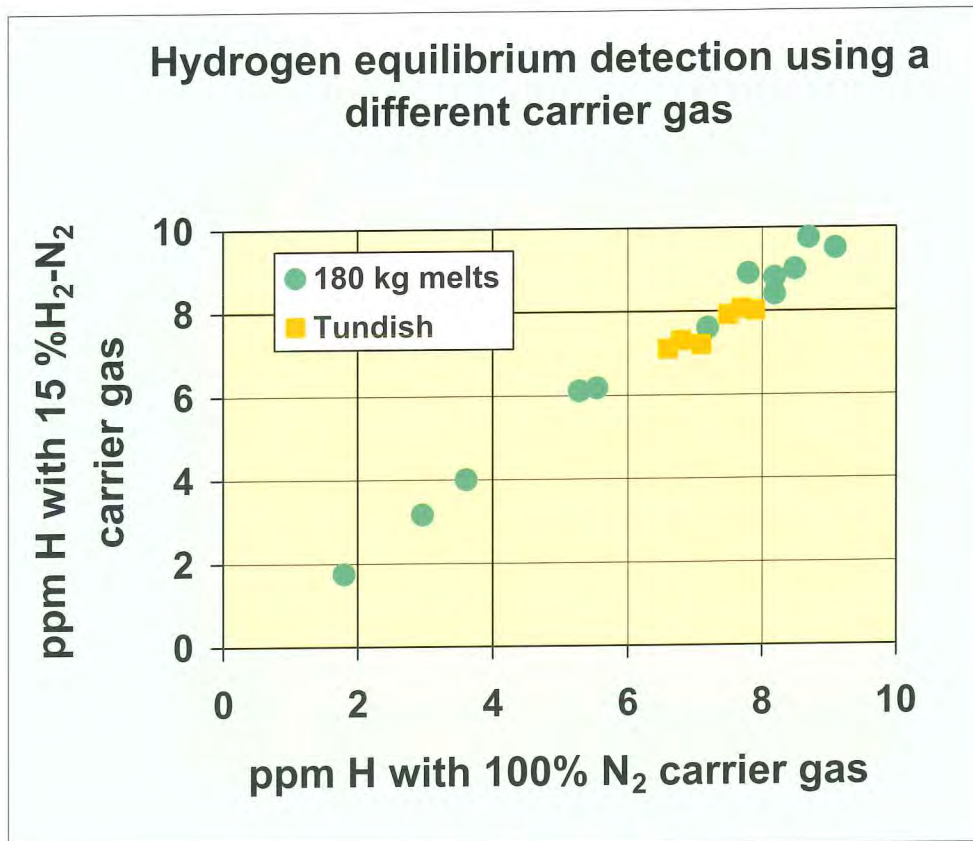
Figure 5: Detection of hydrogen equilibrium using two different carrier gasses[2]

2 Hydris® characteristics

A. Measurement limits

The Hydris® system is able to measure all possible hydrogen contents. The measurement time will increase with higher hydrogen contents. A simple modification of parameters will allow the Hydris® user to optimise his measurement conditions.

B. Application limits

Some problems are to be expected as soon as:
a. The oxygen level exceeds 200 ppm
b. The titanium level exceeds 0.08 %
c. The sulphur level exceeds 0.2 %
d. The bath temperature exceeds 1680 °C

C. Measurement accuracy

The Hydris® system has proven to be a very accurate hydrogen analyser. Experiences in different steel grades have shown an accuracy where 95% of the measurements is lying within a range of ± 5%.
The drift of the thermal conductivity detector remains very limited and can be checked and recalibrated by the use of calibration gasses.
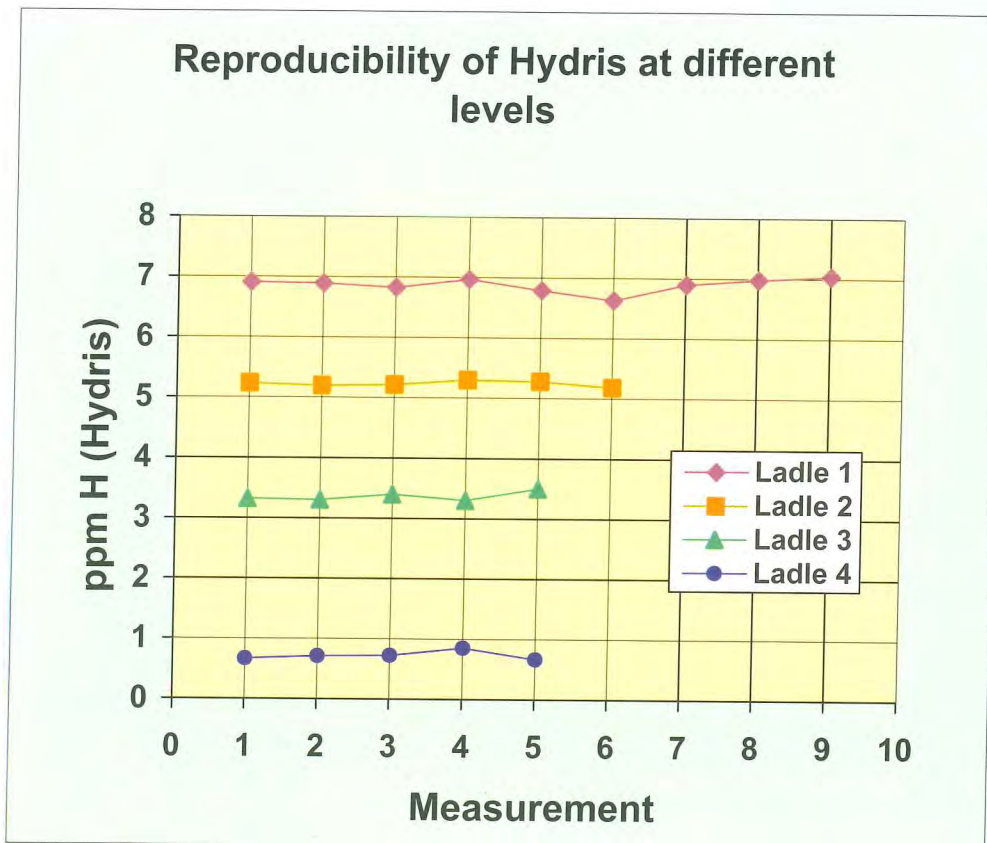
Figure 6: An example of the reproducibility of Hydris® at different hydrogen levels.

3 Hydrogen sampling techniques

It is of interest to compare Hydris® and the pre-existing hydrogen sampling techniques.
Due to the difficulty in the past to obtain a correct hydrogen sample, different techniques have been developed to guarantee the best possible hydrogen sample.

A. Open quenched sampling methods

These methods quench a pin as quickly as possible to "freeze in" the hydrogen.
As these sampling techniques require a lot of different handlings, it is obvious that the possibility of creating errors easily increases.

The copper mould

Liquid steel is sampled by a spoon and cast into a copper mould. The sample is quickly removed out of the mould and cooled in water. The copper mould provides a good initial chill, but requires two skilled operators. The recuperation of the sample out of the mould is also critical.

Pin sample (Ferrostatic filling)

A pin sample is immersed in the steel. The sample is filled by ferrostatic pressure.
This technique can more easily be applied in tundish, but deals with large difficulties in the ladle. As the silica tube only obtains a small initial chill, the cooling is critical[3].
Excessive cooling rates, however, could result in cracks that provide a free surface for hydrogen diffusion and result in too low hydrogen results. If the sample is taken too quickly, piping phenomenon will exist inducing too high hydrogen values[3].

Pin sample (vacuum filling)

A pin sample is immersed directly in the steel. The quartz tube will open and the steel is driven into the quartz tube. The handling to recuperate the sample is, however, identical to the previous techniques. This method provides a quick filling. Premature opening of the sample will, however, result in poor hydrogen readings.

B. Comparison between these different sampling techniques

A comparison between these different open quenched sampling methods shows that when using different techniques, very different hydrogen results can be obtained.
Figure 7 compares the hydrogen analyses of a copper mould with ferrostatic filled hydrogen samples. Figure 8 shows the comparison between ferrostatic filling and vacuum filled samples.
The experience of the operators taking the samples is the most critical parameter.
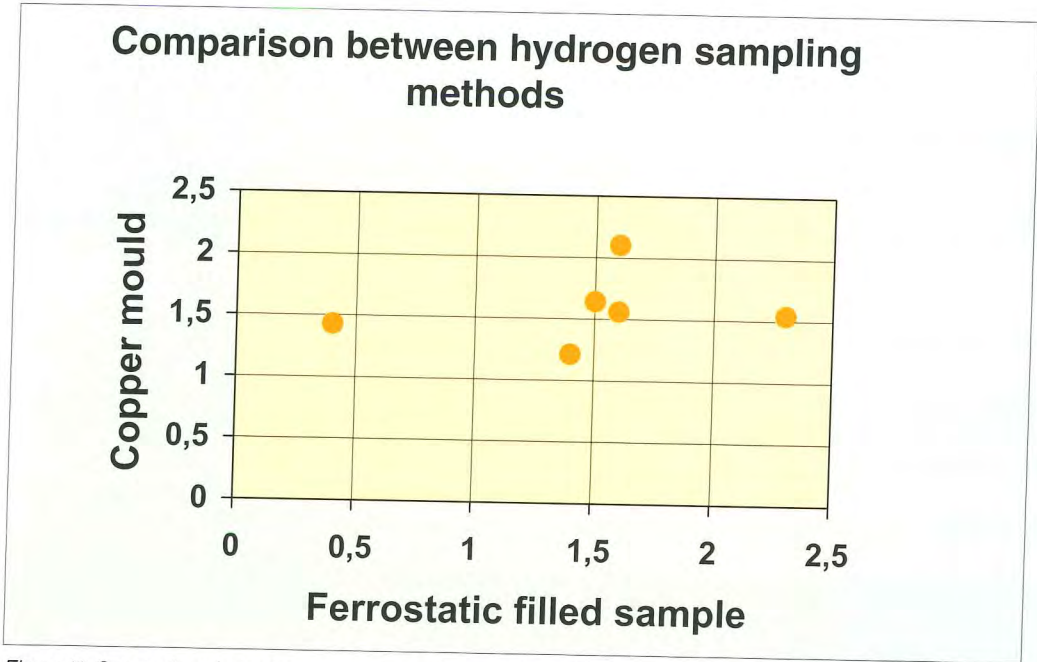
Figure 7: Comparison between copper mould (standard steel plant practice) and ferrostatic filled sample. The poor experience of the operator using ferrostatic samples results in scattered analyses.
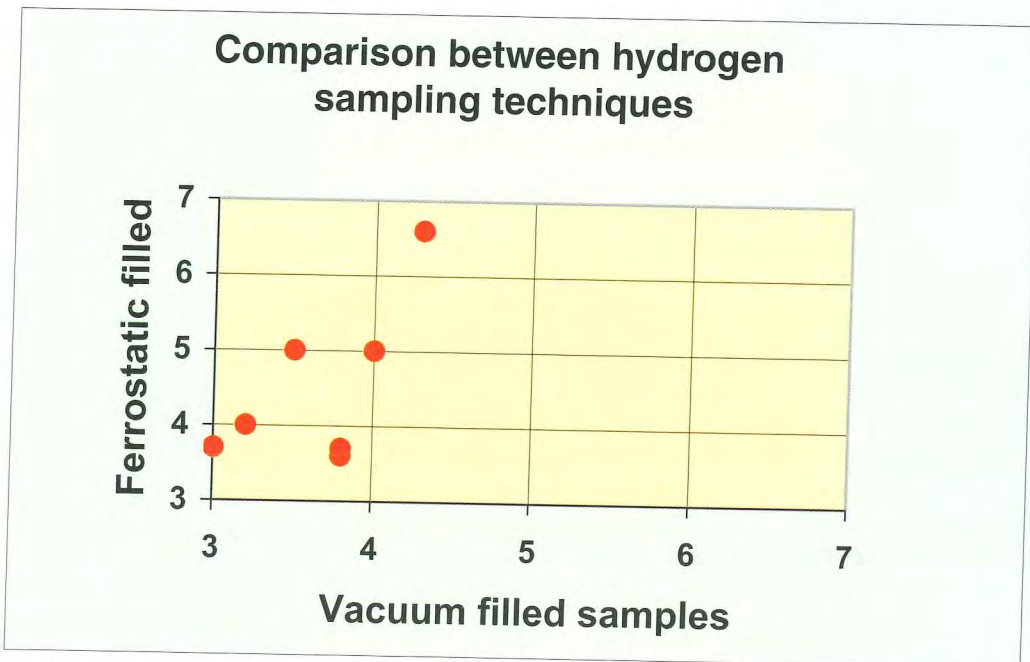

Figure 8: Comparison between a ferrostatic filled hydrogen sample and a vacuum filled sample. The ferrostatic sample will, in this example, result in higher hydrogen contents.
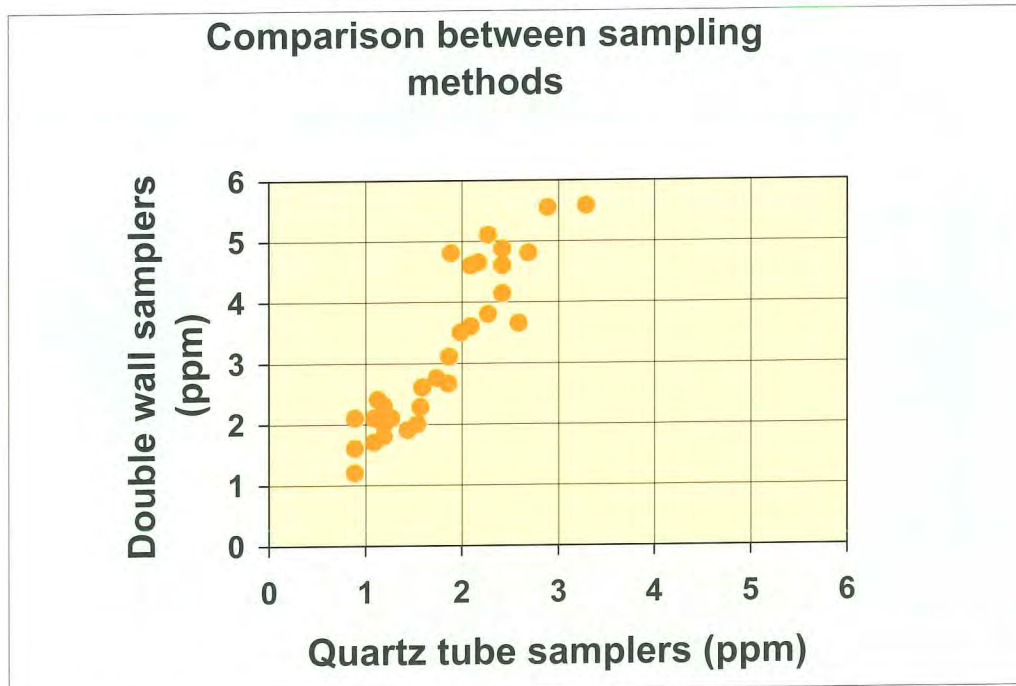
Comparison between sampling methods

Figure 9: Comparison between quartz tube samplers and double wall samplers [4]

C. Double wall samplers

The double wall sampler analyses gaseous hydrogen entrapped while diffusing from a cooling sample and the remaining solid sample.
Comparisons between this technique and the open quenched samples show results with ratios between 1.3 to 2 times[4].
This is explained by premature diffusion of hydrogen in the diffusion chamber during immersion before filling of the sample[5].

D. Comparison of Hydris® with the hydrogen sampling techniques

As handling practice and experiences differ from steel plant to steel plant, it is impossible to draw a general conclusion.
Different examples are described yet, where as well good as bad correlations are shown between Hydris® and various lab results.

Analysing non-degassed melts

Figure 10 shows a comparison between Hydris® and a pin sample in a steel plant where hydrogen sampling is not a standard practice. It clearly shows that serious errors will easily be introduced due to poor sampling techniques.
Even if hydrogen sampling is a standard practice, diffusion of hydrogen cannot always be avoided, resulting in too low hydrogen. Figure 11 shows examples of analyses of two different labs, showing too low hydrogen values. In the first case (lab 1), the difference between lab and Hydris® increases as soon as hydrogen (by Hydris®) exceeds levels of more than 4 ppm. In the second case, the sampling is being taken so ineffectively, that all hydrogen is diffused before being analysed.

This figure also shows that using different handling techniques will result in different hydrogen diffusion patterns within the pin sample and will, on its turn, affect the comparison between Hydris® and lab.

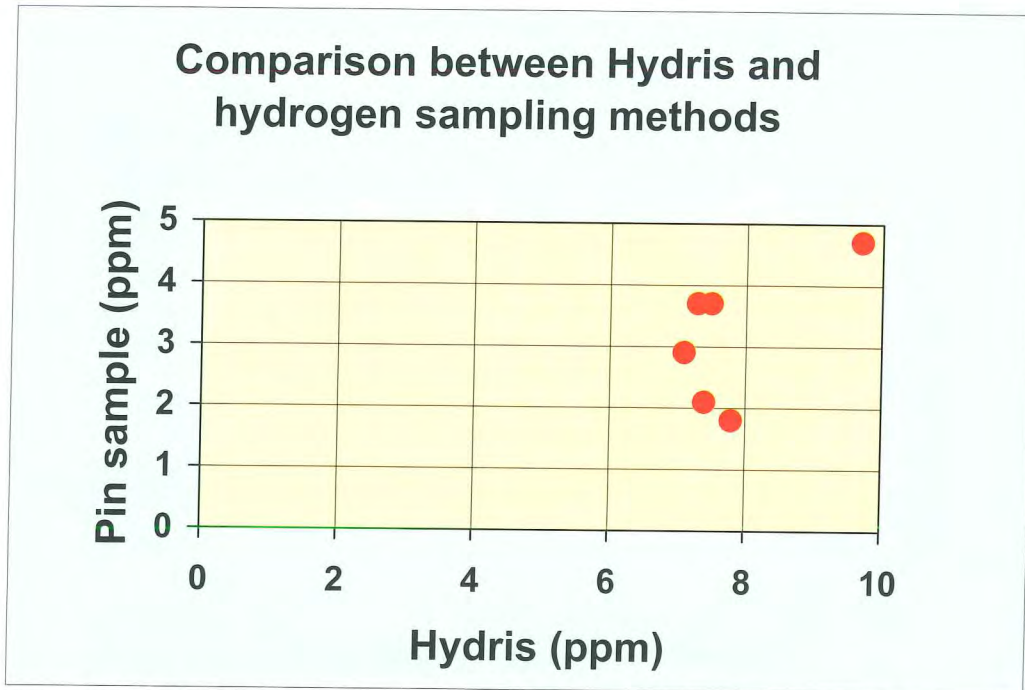Figure 10: Example of a comparison between Hydris® and pin samples, taken in a steel plant where hydrogen analyses are not standard practice.
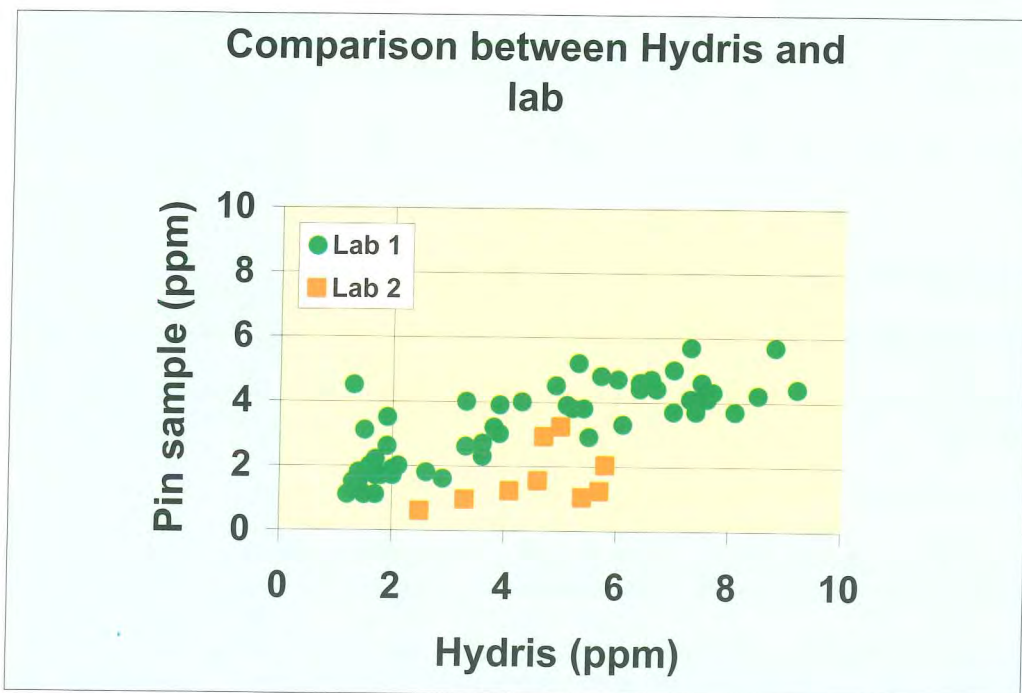
Figure 11: Different sampling techniques will result in different comparisons between Hydris® and lab.

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 pick-up when sampling in a spoon, but also due to the occurrence of piped samples and slag entrapment.

For very low values (<1 ppm), 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].

Figure 12 shows the comparison between Hydris® and two labs for low hydrogen values. Both steel plants use the copper mould technique. Despite of the use of an identical sampling method, as well good as poor correlations are found.

However, the figure shows that in both cases the lab values are higher than Hydris®.

Figure 12: Comparison between samples obtained by the copper mould method in two different steel plants and Hydris®. Lab 1 shows a good correlation. Lab 2, however, tends to give too high hydrogen values

II. HYDRIS® APPLICATIONS IN MODERN STEEL MAKING

1. Primary steel making

A. Electric Arc Furnace

Measuring conditions

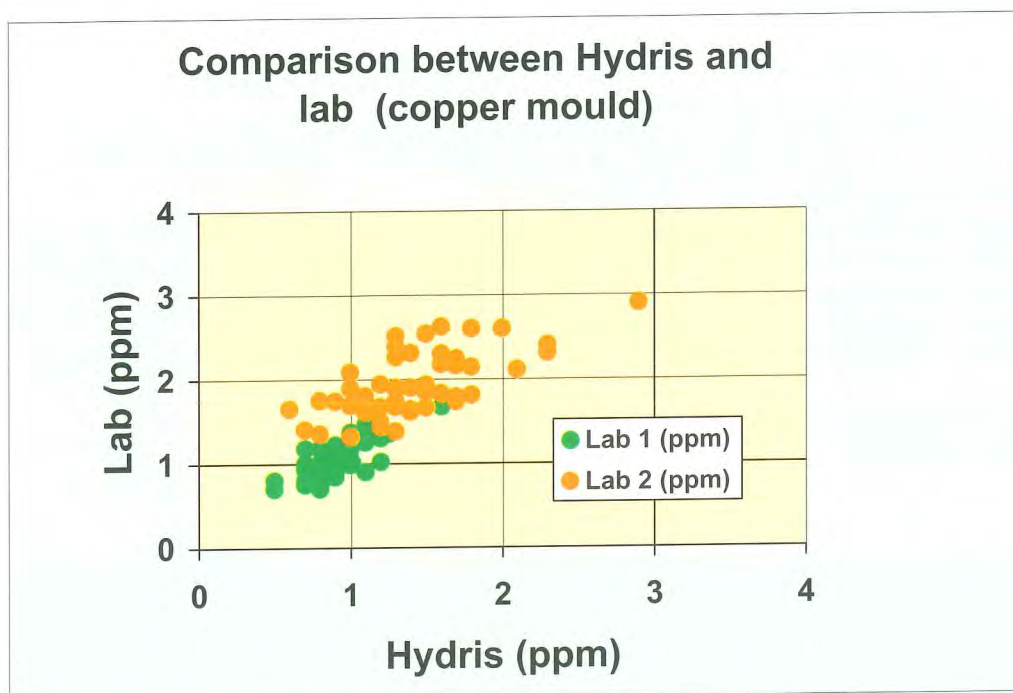Hydris® measurements in an electric arc furnace are lying within the possibilities of the Hydris® system, although not without any difficulties and with special precautions

* As slag build up in the EAF furnace could disturb proper immersion of the Hydris® lance into the melt
* As the lance needs to be shielded from heat and radiation
* As an optimal lance design is required to allow the easiest passage into the furnace to obtain a vertical immersion

Influence of the process on the hydrogen level

The hydrogen levels obtained at the end of an electric arc furnace are in average between 2 to 4 ppm and higher in comparison to top blowing converters.
The use and combination of following parameters will determine the final hydrogen content:
* The use of lime, very sensitive for atmospheric moisture
* The amount of charge carbon and oxygen blowing:
  The hydrogen level will automatically reduce during oxygen blowing. Figure 13 shows an example of a melt where in a small induction furnace (150 kg), on different time intervals, oxygen is blown in the melt. Initially, some hydrogen pick-up due to the stirring of the small steel bath, takes place. 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 of the electrodes
* Atmospheric conditions

The use of the Hydris® measurement

The measurement of Hydris® in the electric arc furnace could be used to determine the different sources of hydrogen-pick up at the earliest stage of steel making.
The use of Hydris® as a routine- instrument is unlikely, as measurement conditions are quite difficult.

Influence of oxygen blowing on the hydrogen content
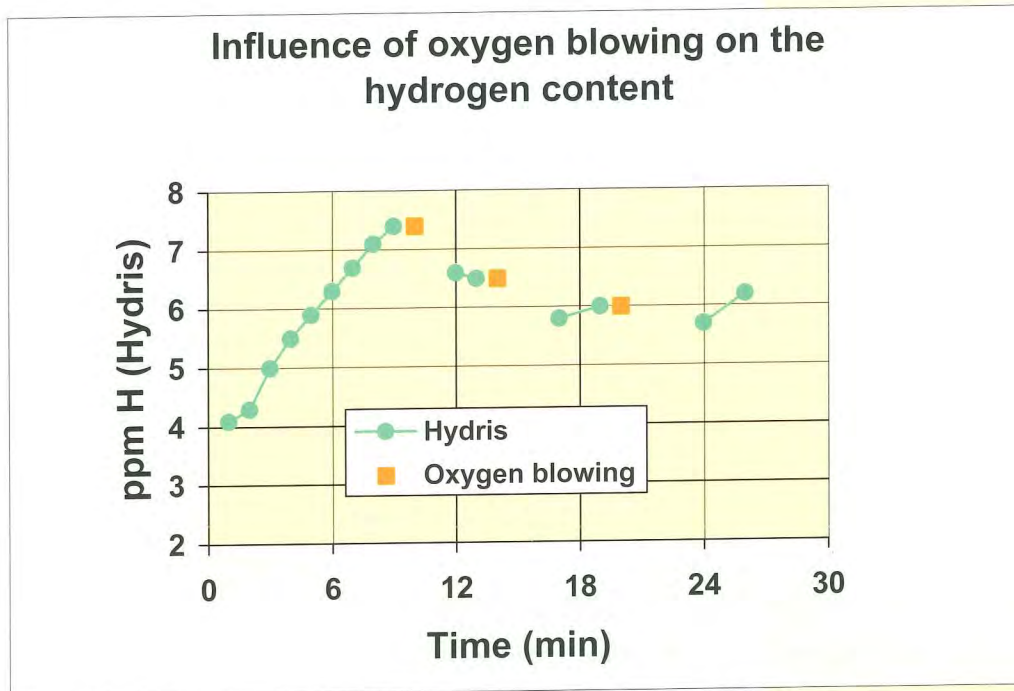
Figure 14: Influence of oxygen blowing on the hydrogen level in a small induction furnace. The hydrogen level clearly drops after oxygen blowing.

B. Converter shops

Measuring conditions:

Normal practice does not allow the Hydris® user to carry out measurements in the converter,
* Due to excessive heat and a longer measurement time compared to temperature and oxygen measurements.
* Due to the high oxygen level and formation of CO gasses. This very intensive stirring will reduce the hydrogen level in the steel bath.

Top blowing processes

Hydrogen levels at end of blowing should be lying around 1 to maximal 2 ppm.
Burning through of the oxygen lances can, however, result in a serious hydrogen pick-up.

Bottom blowing processes

When bottom blowing processes are being used, the oxygen is blown through the bottom. To avoid excessive heat near the blowing tuyere, some hydrocarbon cooling gasses 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 gasses and the removal of gasses from the metal together with CO bubbles. When the heat finishes a very low carbon content, the concentration of CO in exhaust gasses becomes very low and the partial pressure of H_2/H_2O gradually increases. Blowing with inert gasses before tapping should, however, reduce the hydrogen content.

Figure 14 shows how the hydrogen content will increase as soon as very low carbon levels are obtained at the end of blowing[7].
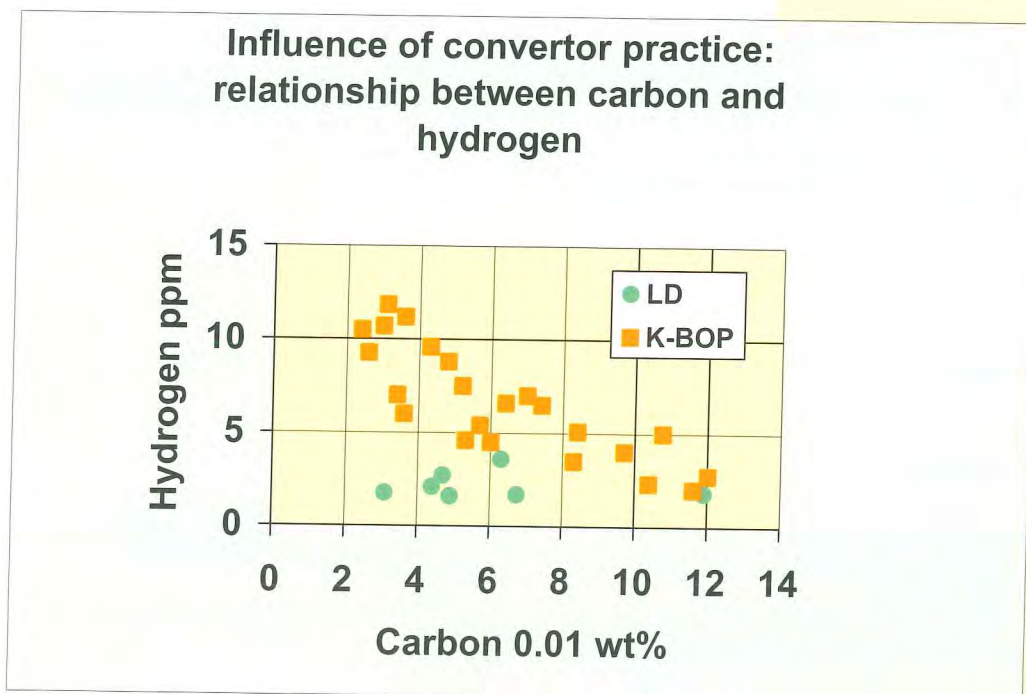

Figure 14: influence of converter practice on the final hydrogen content[7].

Steel makers should also take into account hydrogen pick-up phenomena when tapping the steel into a ladle.

Using unpreheated ladles, new linings and lime (or other additions) could result in high hydrogen levels in the ladle, even before ladle treatment.

A. Measuring conditions

Ladle stirring stations do not impose specific measures for the Hydris® measurement.
One should, however, take care that

*   The Hydris® measurement is not made during argon or nitrogen stirring. Pick-up of these gasses will disturb the Hydris® reading. Optimal measurements can be obtained when the operator waits one minute after the end of intensive blowing, to enable small slag particles to float to the surface, instead of sticking on 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 made.
*   Measurements are made as vertical as possible

For the ladle furnace:

*   Sometimes specific measures need to be taken to avoid excessive heating of the lance during measurement. Optimal design of the lance and the use of telescopic cardboard tubes will protect the lance very well.

B. Influence of the ladle stirring/ ladle furnace process on the hydrogen level

The hydrogen level will rise 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 serious pick-up of hydrogen
*   Bad storing conditions of scrap or the use of rusty scrap will also result in an increase of hydrogen (see figure 15)
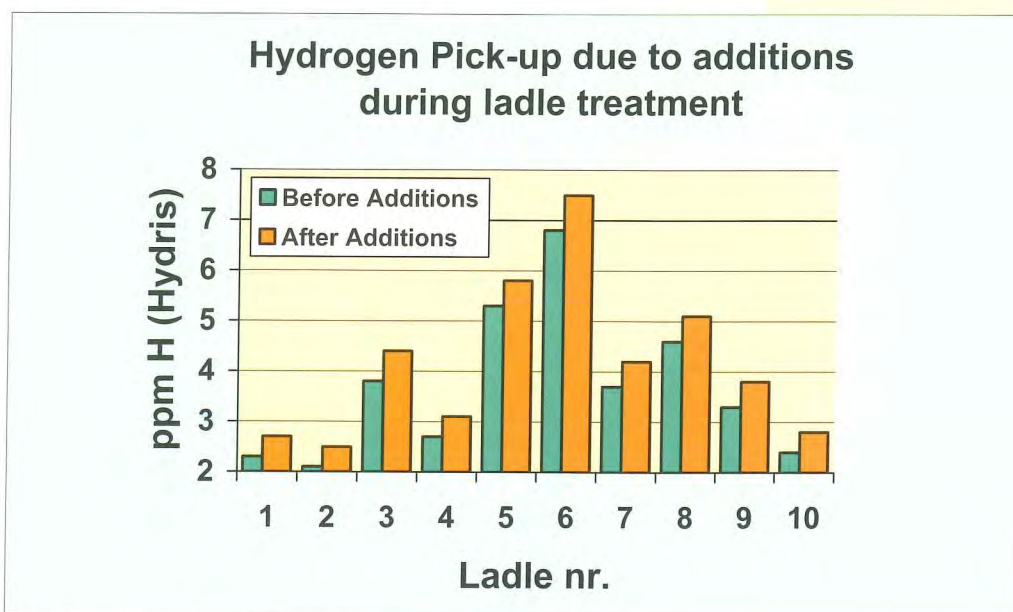

Figure 15: Hydrogen pick-up during ladle treatment in a stirring station.
Additions consist out of scrap, aluminium wire and ferroalloys.

* The use of ferroalloys will also affect the hydrogen content
* Aluminium and CaSi-wire will only result in a very small input of hydrogen (maximal 0.1ppm) (figure 16)
* Heating of the ladle results in a small hydrogen pick-up, especially if the heating remains moderate (figure 17):
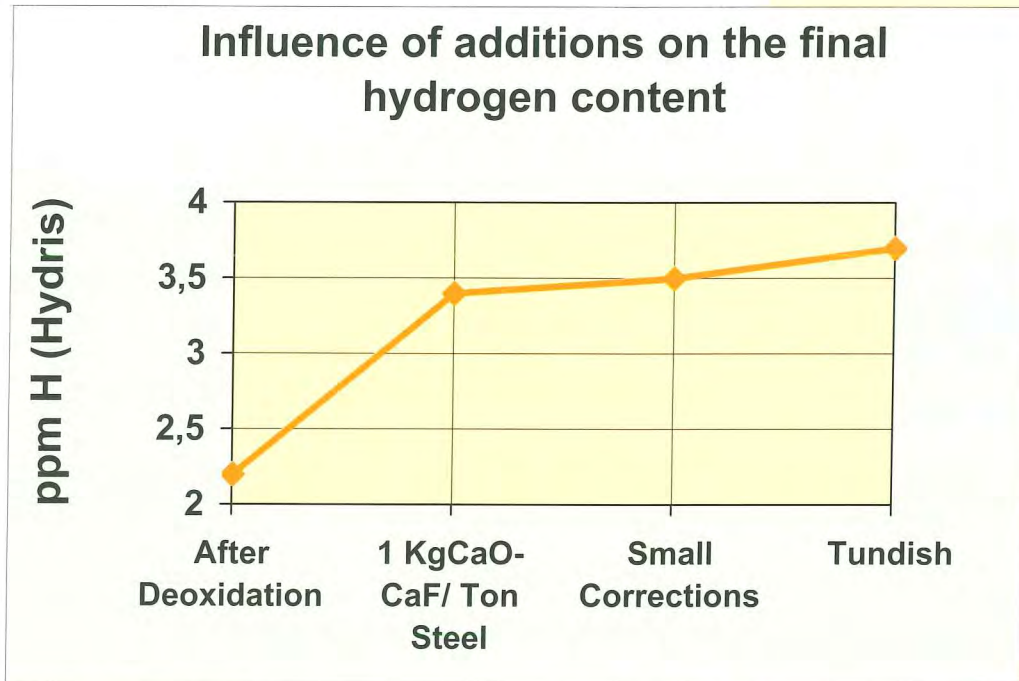
Influence of additions on the final hydrogen content

Figure 16: Sum of total hydrogen pick-up in a ladle (low carbon sheeth steel) until casting.
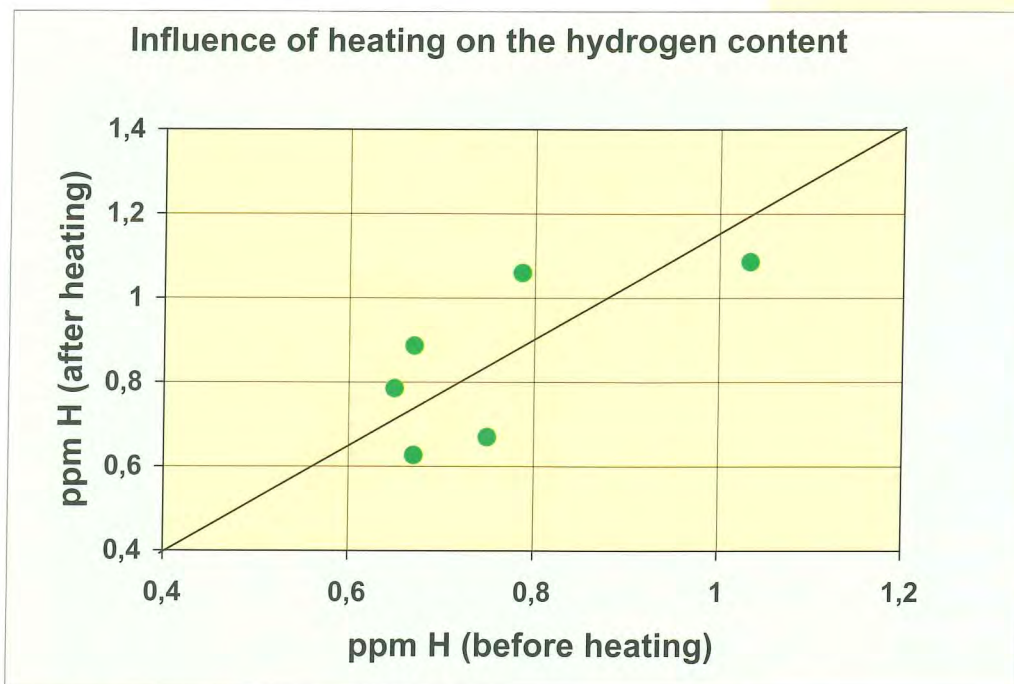
Influence of heating on the hydrogen content

Figure 17: Influence of heating in the ladle furnace on the hydrogen content.

C. Ladle (furnace) applications for Hydris®:

The Hydris® measurement can be used:

1. To optimise process control

* By defining the hydrogen pick-up of different additions
* Minimising hydrogen pick-up by quantifying hydrogen pick-up of additions
* Define hydrogen level before casting to control hydrogen pick-up in the tundish

2. As a routine instrument

* By determining the necessity of an additional degassing step
* To determine the most optimal sulphur content as function of the measured hydrogen content (figure 18)

In the appendix, an example is found of a mathematical model calculating the contributions of the different additions during ladle treatment that has been developed by Mr. Varcoe and co-workers of BHP-Steel Australia.
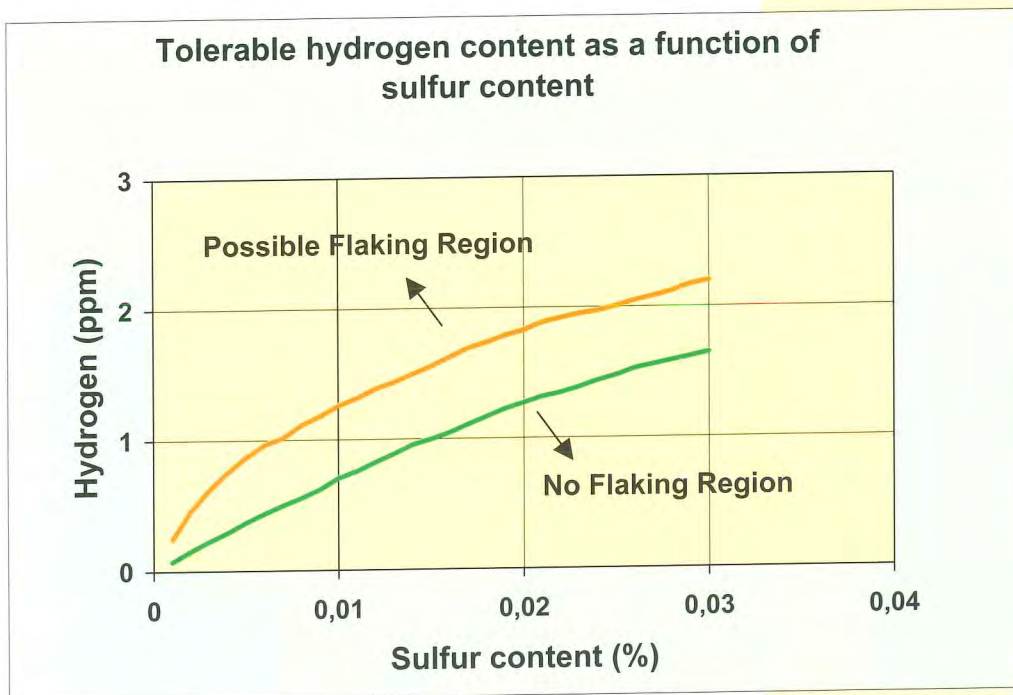

Figure 18: An example, found in literature, of a diagram illustrating the optimisation of the hydrogen/sulphur ratio to avoid flaking [8]

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

3. Degassing Processes

A. Measuring conditions

The general guidelines for Hydris® obviously remain valid for all degassing applications:
1. Try to measure as vertical as possible
2. Hard slag must be crushed before measuring

Distinction should be made between different degassing systems:

1. The RH- process
   The specific circumstances of the RH-process allow Hydris® users to carry out hydrogen measurements during degassing.

2. DH, VD and VAD degassing processes
   Due to the movement of the bath level (DH-system) during the process or the complete sealing of the ladle in tank degassers (VAD), it is impossible to carry out a Hydris® measurement during degassing. The hydrogen measurement can only be made 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 made.

B. Influence of the degassing parameters on the final hydrogen content

Degassing time

The hydrogen level will decrease with increasing degassing times. However, the reduction in hydrogen will start to slow down as soon as hydrogen levels are being reached of 2 ppm.
As soon as this level is reached, other parameters will become more important. Figure 19 shows us the hydrogen decrease in time at an RH-degasser.
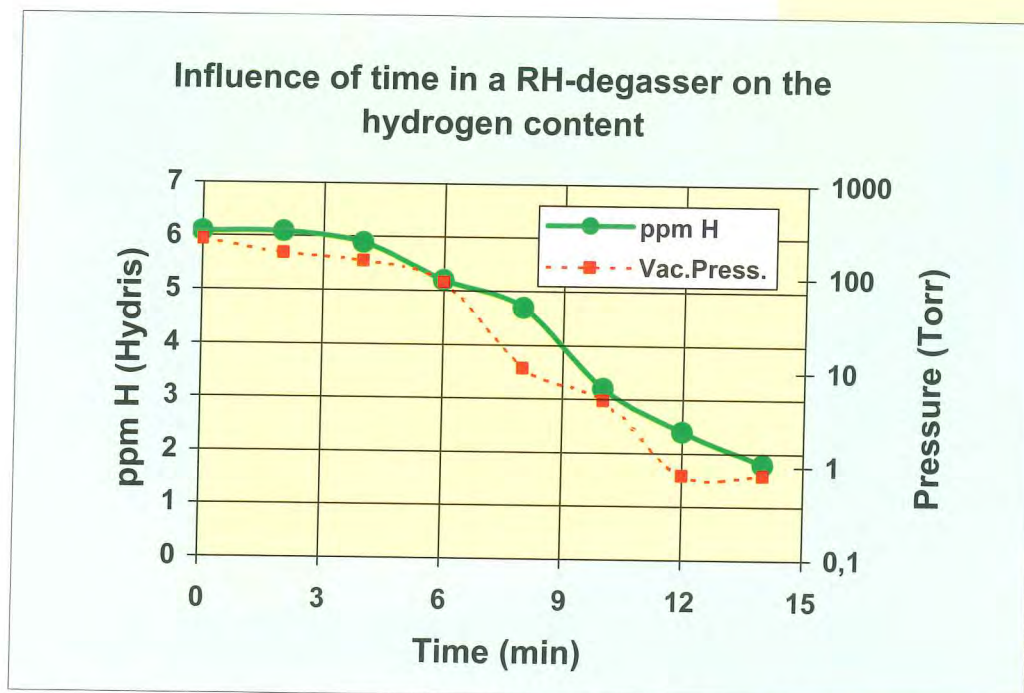

Figure 19: Influence of degassing time on final hydrogen concentration at the end of the treatment
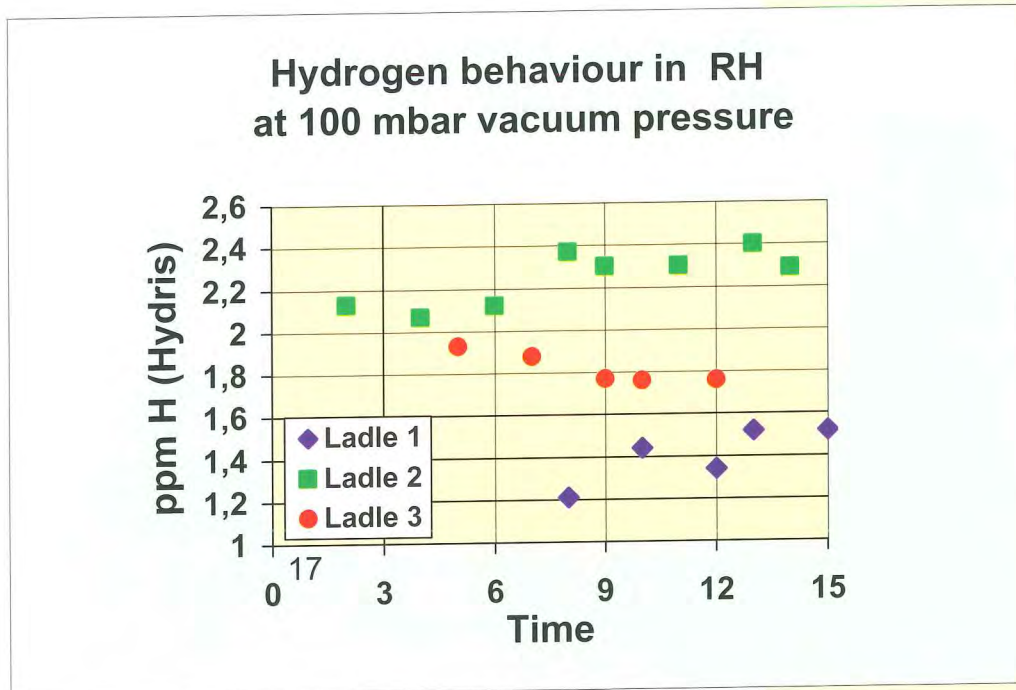
Hydrogen behaviour in RH at 100 mbar vacuum pressure

Figure 20: the hydrogen content will not decrease if the applied vacuum pressure is too high

Vacuum pressure

A good maintenance of the degassing unit is crucial to ascertain very low hydrogen levels. Final hydrogen contents below 1 ppm can only be achieved with vacuum pressures of below 1 mbar .
Figure 20 shows that the hydrogen level will not decrease if a working pressure of 100 mbar is used.

Initial hydrogen level

If only short degassing treatments are applied, it is essential to avoid too high initial hydrogen levels (figure 21). Valuable time will be lost to eliminate the superfluous hydrogen. The initial hydrogen level is, however, less critical if longer degassing times are applied (figure 22).
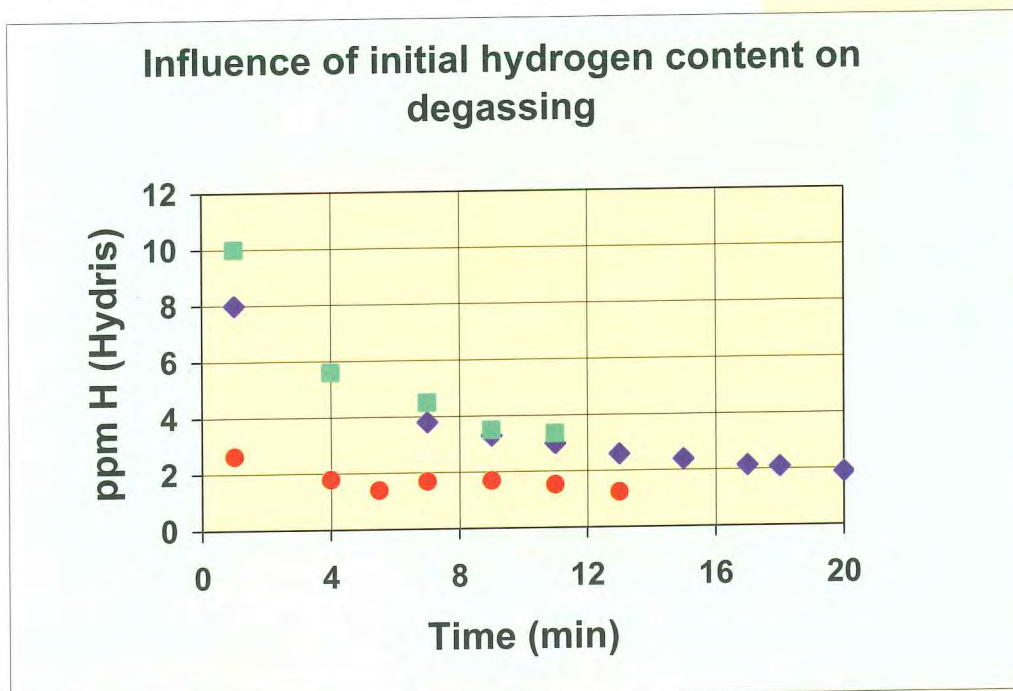
Influence of initial hydrogen content on degassing

Figure 21: The initial hydrogen becomes critical for short degassing treatments
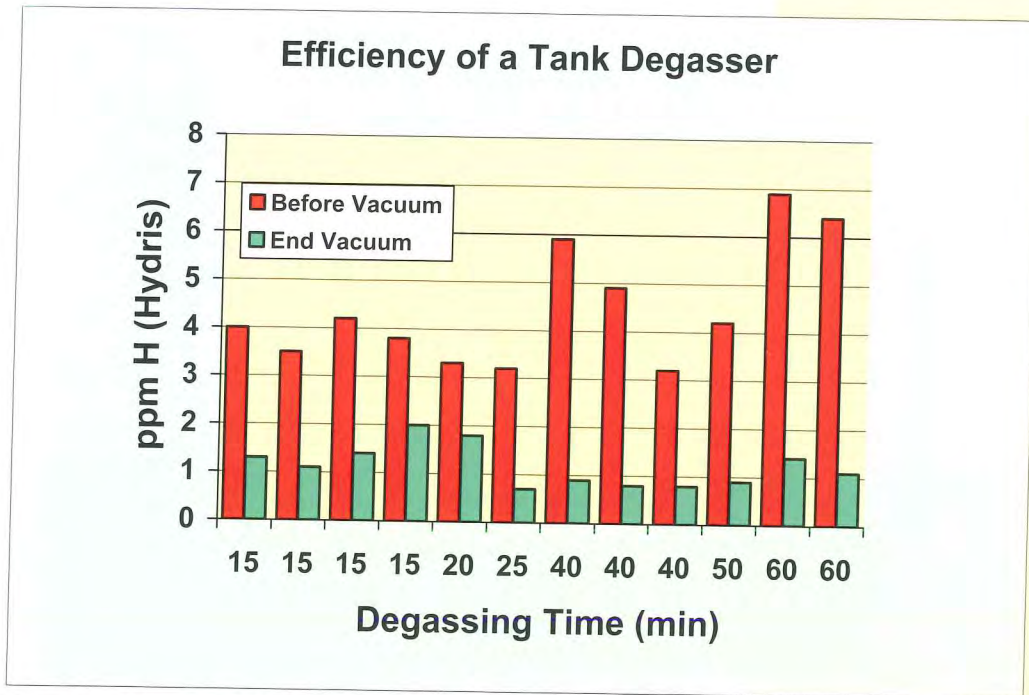
Efficiency of a Tank Degasser

Figure 22: The initial hydrogen content is less critical for long degassing treatments.

The use of additions

Keep in mind that additions of ferroalloys, lime... at the end of the degassing treatment might spoil the degassing efforts as they can rise the hydrogen level due to hydrogen pick-up.
Figure 23 shows the hydrogen pick-up after additions of some alloys shortly before the end of the degassing treatment in an RH.

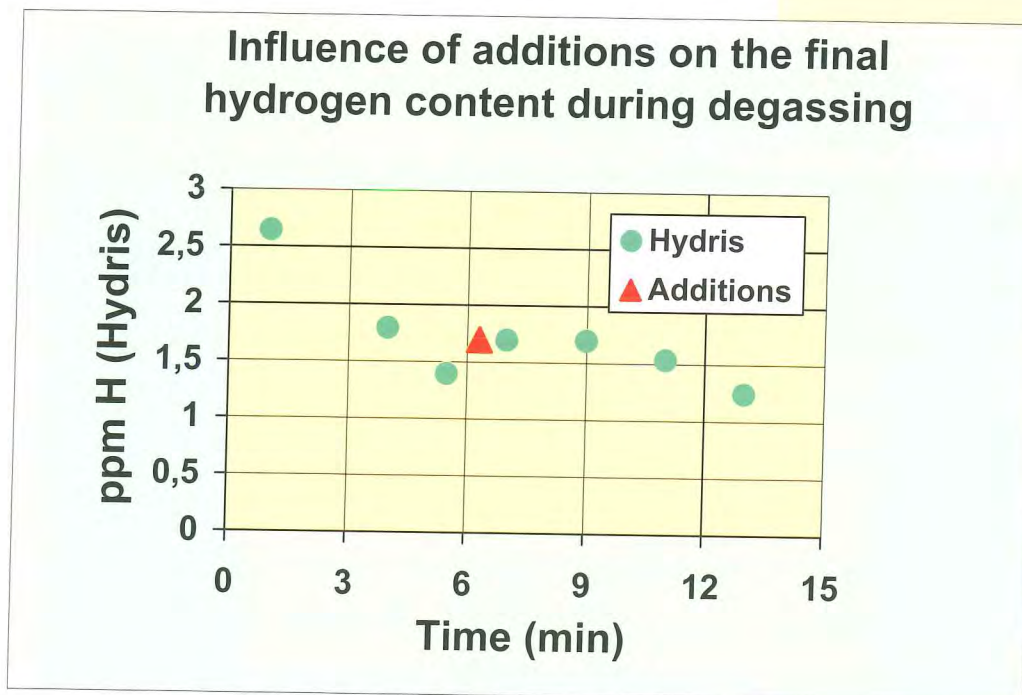**Influence of additions on the final hydrogen content during degassing**

Figure 23: Hydrogen pick-up due to additions made during degassing

Volume of inert gas blowing

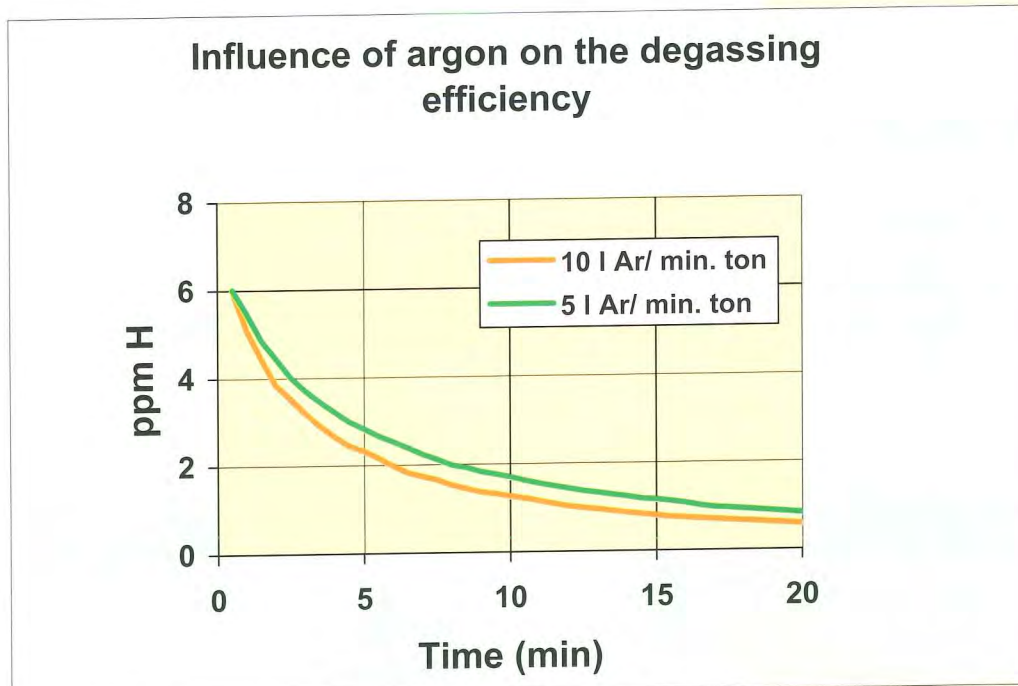The hydrogen reduction can be maximised by increasing argon flow (Figure 24).

Influence of argon on the degassing efficiency

Figure 24: The hydrogen level decreases easier by increased argon flow [8].

The type of steel grades

Some steel grades require longer degassing times to ascertain very low hydrogen levels.
Figure 25 compares the final hydrogen level of low alloyed carbon grades to a few stainless steel grades.
Degassing of stainless steel grades result in hydrogen levels around 1.4 ppm, whereas low alloyed grades easily come down to 0.7 ppm

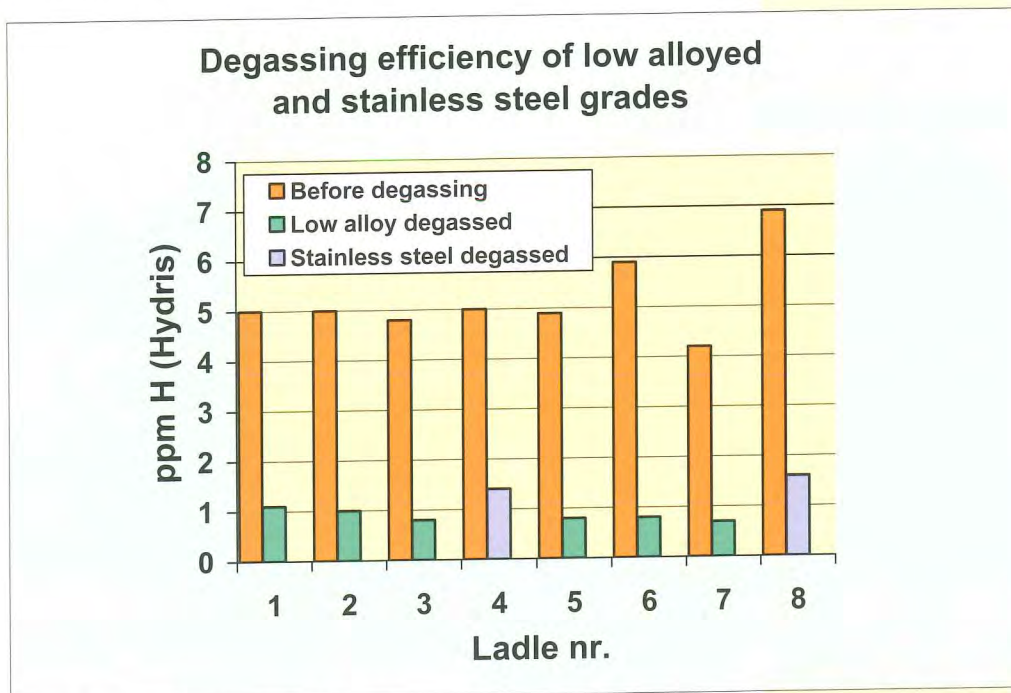**Degassing efficiency of low alloyed and stainless steel grades**

Figure 25: This graph compares the degassing efficiency related to the type of steel grade. The figure clearly shows that degassing of stainless steel grades results in higher final hydrogen contents.

C. Hydrogen degassing models

The accuracy of Hydris® enables steel plants to work out degassing models to determine the optimisation of degassing parameters.

In the first model, developed by A.Jungreithmeier[9] for Böhler Kapfenber, three main parameters were selected: Initial hydrogen level, minimal vacuum pressure and argon stirring period.

The second example[10] shows the excellent correlation between the results predicted from a degassing model, developed by Irsid and actual Hydris® measurements.
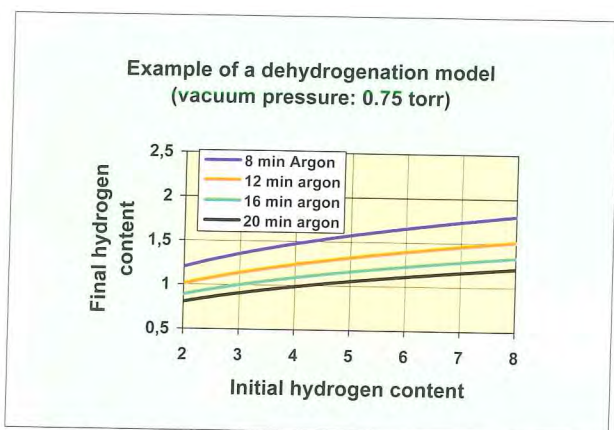
Figure 26: First example of a dehydrogenation model based on Hydris® measurements[9]
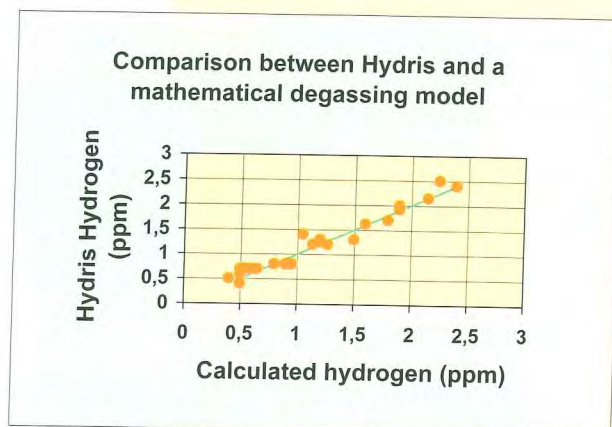
Figure 27: Example of an excellent correlation between the results predicted from a degassing model, developed by Irsid and actual Hydris® measurements[10]

D. Degasser applications for Hydris®

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

Labeling the product
Immediate hydrogen measurement at the end of the degassing cycle provides the steel maker with an improved quality monitor prior sending the ladle to the caster or ingot station. This procedure impises responsibility to the degassing unit and influences the final quality.

4. Continuous Casting

A. Measuring conditions

The Hydris® measurement in the tundish does not impose specific measures for the Hydris® measurement.
* One should however take care that the Hydris® measurement is made as vertical as possible. This can be done by optimising the design of the lance and the use of the smaller Hydris® probes
* Excessive leakage of the argon shielding gasses of the nozzle must be avoided

B. Influence of continuous casting on the final hydrogen concentration

Hydrogen pick-up in tundish

A pick-up of hydrogen in the tundish can hardly be avoided.
At the start of a new sequence, special care must be taken to reduce the hydrogen pick-up as much as possible. Despite of the preheating of the tundishes before the start of casting, the moisture deeper in the lining will slowly release hydrogen that gradually will be picked up by the steel. Figure 28 shows a typical example that shows the linear decrease of the hydrogen concentration in the tundish.
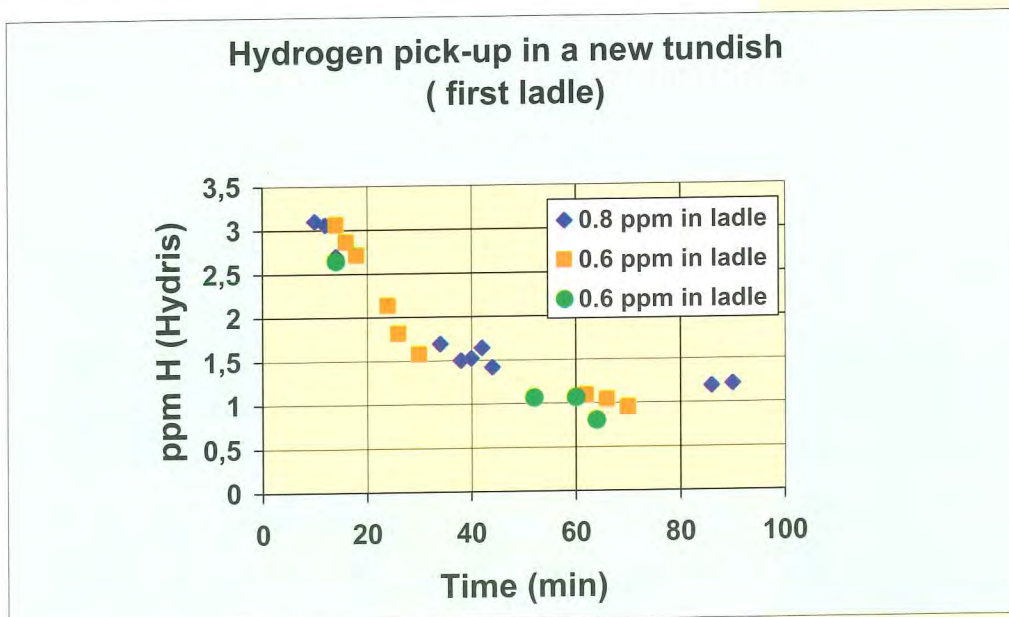

Figure 28: Linear decrease of the hydrogen content in a new tundish

The accuracy of Hydris® allows the user to obtain very specific data characterising the pick-up in the tundish. Figure 29 shows that for a particular tundish, the hydrogen level slowly increases to a maximum (e.g. 15 minutes after the opening of the ladle), and decreases linearly to obtain a stable value after 30 minutes.
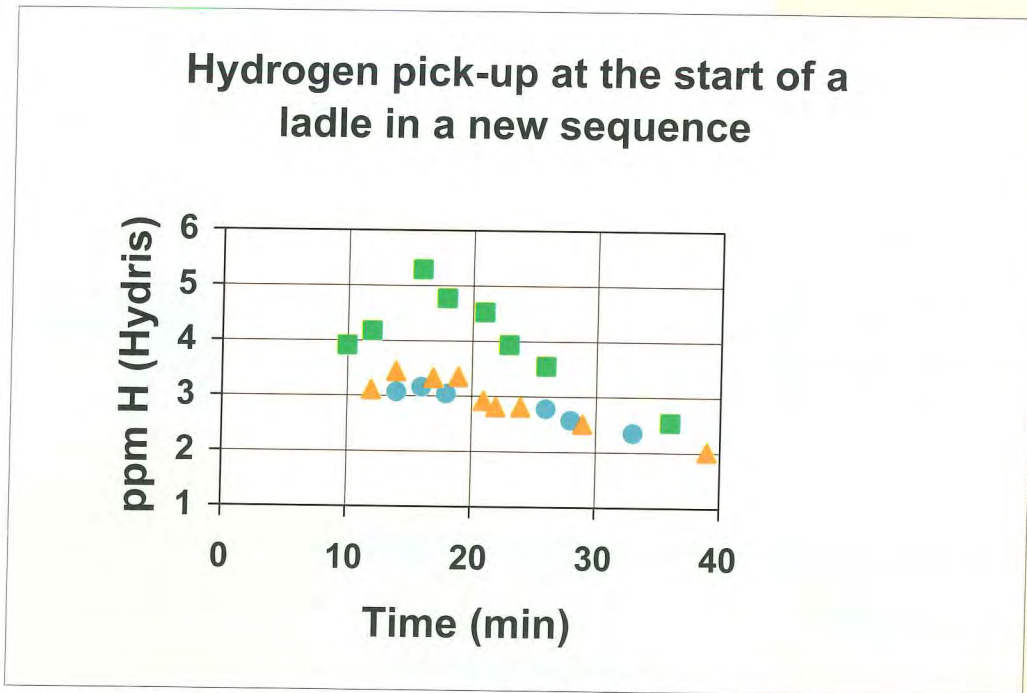
Figure 29: Detailed description of the hydrogen pick-up with the Hydris®

From the second ladle onwards, one should count with a pick-up of around 0.3 ppm average under normal conditions. It is of course necessary to take into account the hydrogen level of the previous ladle (figure 30) However, if the tundish runs empty during a ladle change, this could result in a small hydrogen pick-up at the start of the new ladle. The hydrogen pick-up remains moderate in large tundishes, but can become important in very small tundishes. Depending on casting speed and tonnage of tundish, this could take some time (Figure 31). The pickup in a large tundish will be much smaller.
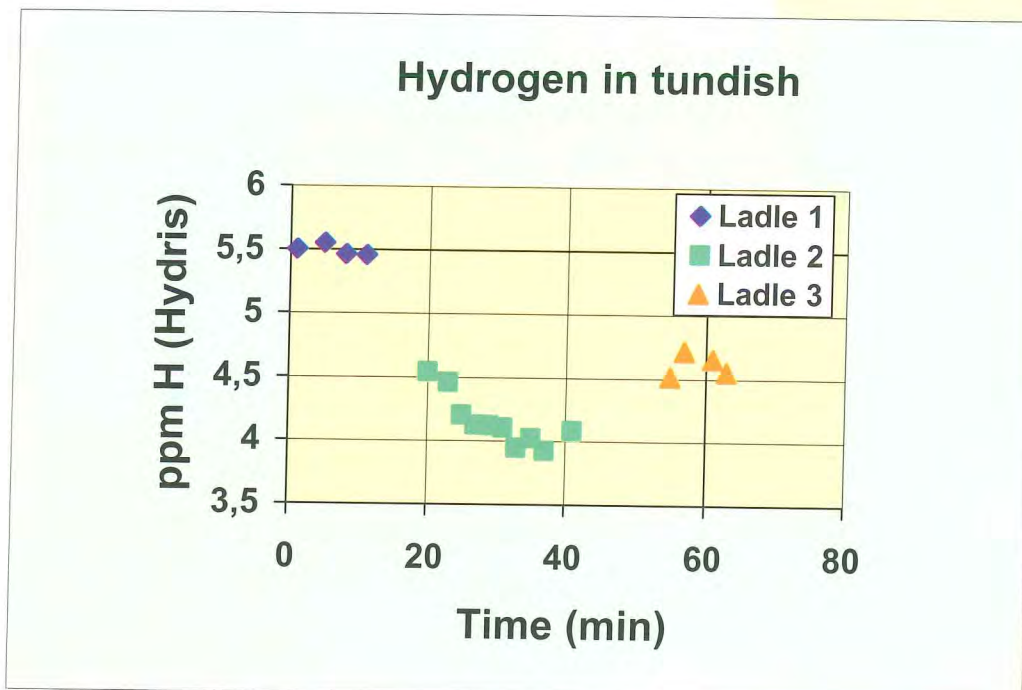

Figure 30: The ladle change occurred after 15 minutes. However, it took about 15 minutes casting before the intrinsic hydrogen level of ladle 2 was found. Total casting time of a ladle is 35 minutes.
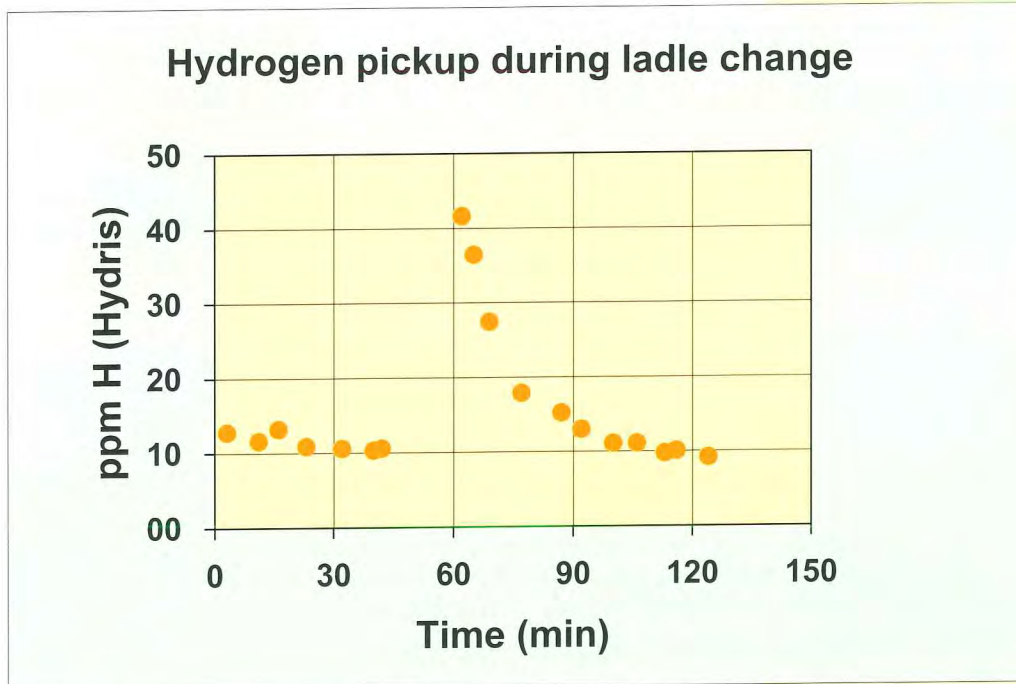
Hydrogen pickup during ladle change

Figure 31: The hydrogen pick-up during ladle change in a small tundish (8 tonnes)

Breakout detection

Various workers have confirmed a relation between the hydrogen content in the steel and breakouts on the continuous caster[11]. Related breakouts are of the sticking type and 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 is increased (figure 32). The risk of breakouts becomes very critical as soon as the hydrogen level exceeds 9 ppm. These types of failures can hardly be detected by pin samples as their reliability drastically decreases for high hydrogen levels.
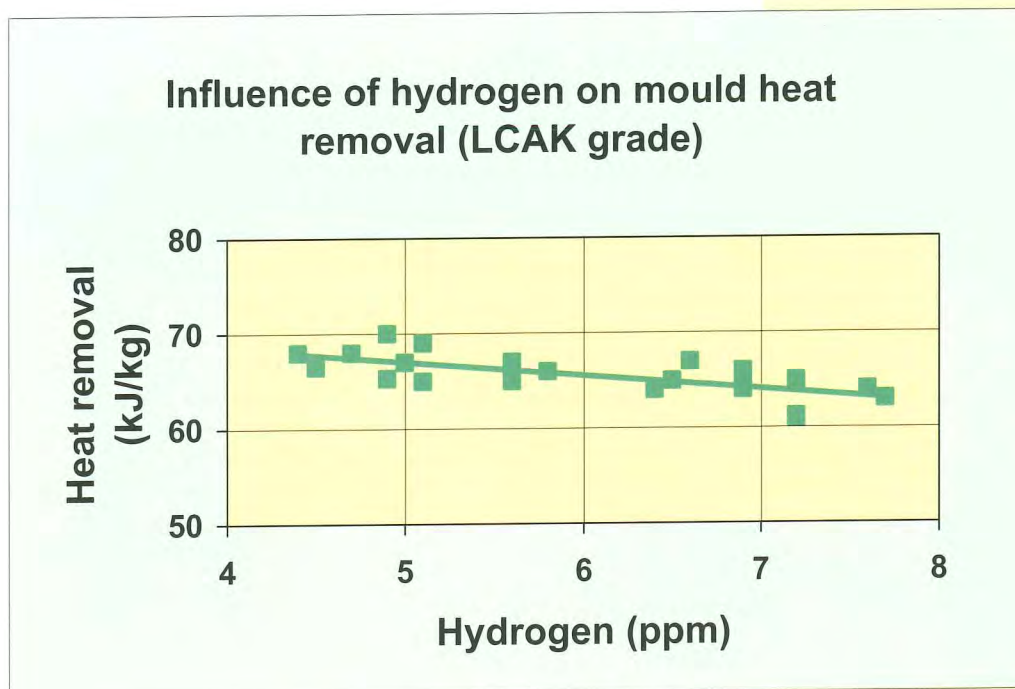
Influence of hydrogen on mould heat removal (LCAK grade)

Figure 32: Increased hydrogen contents result in poorer heat removal and can result in tundish breakouts[11]

Thin slab casting

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

C. Tundish applications for Hydris®

Hydris® and quality control

Hydrogen pick-up in the tundish cannot be avoided. The accuracy of Hydris® allows,
however, the steel maker to minimise hydrogen pickup by optimising his tundish practice.
The accuracy of Hydris® ensures the steel maker the confirmation of required
standards. This confirmation is independent on the handling practice of the operators.
The accuracy of Hydris® allows him to work on more tight schedules and avoids unnecessary thermal treatments that cost money and complicate production processes.

Hydris® and breakouts

A direct hydrogen determination at the start of casting will inform the steel maker immediately on the risk
of eventual breakout danger. The steel maker can decide either to continue casting or to break off the
casting sequence.

Hydris® and thin slab casting

A direct hydrogen determination will inform the steel maker on 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 inform on the necessity of additional annealing treatments.

5. Ingot casting

A. Measuring conditions

The Hydris® measurement in the ingot does impose specific measures for the Hydris® measurement.
* Due to the low superheat, flushing times during measurement should be increased even up to 20 seconds.
* Measurement should be made as late as possible to obtain homogeneous conditions. However, take note of the temperature loss during casting.

B. Influence of ingot casting on the final hydrogen concentration

Due to specific measures taken by steel makers, the hydrogen pick-up in ingot remains small. Experiences at different steel plants show that an average pick-up up to 0.5 ppm can be expected.

C. Ingot casting applications for Hydris®

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

Hydris® and process control
The accuracy of Hydris® ensures the steel maker the confirmation of required quality standards. This confirmation is independent on the handling practice of the operators.
The measured hydrogen levels will on their turn decide on the annealing process to be applied after casting.

III. Hydrogen in steel

Hydrogen is the cause of a number of steel defects and cases of failure. These defects are caused by internal pressures developed when hydrogen atoms pair to form the stable higher volume molecule H_2. The incidence is increased by increased hydrogen content and plate thickness.

A. Flakes

One of the most harmful effects of hydrogen is the formation of flakes. They appear below 200°C and lead to fissure failures in steel constructions. Preferred locations for flake formation are around inclusions and areas of martensite or segregation. Flakes are not observed in unalloyed steel, but are easily formed in manganese, chrome and nickel steels. Figure 33 illustrates the influence of manganese on the occurrence of flakes[12] . Increasing research has also initiated the trend towards very low sulphur grades to reduce sulphur- related cracks. As sulphur content is reduced drastically, the steel becomes very clean with only very limited impurities. As hydrogen tends to diffuse to these impurities, but only a few of them are available, the critical limit of hydrogen concentration around these few impurities is quickly exceeded resulting in cracks. Prevention of flakes is crucial e.g. for heavy plates, rails, and pipelines.

Figure 33: Increasing manganese contents require special care for hydrogen [12]
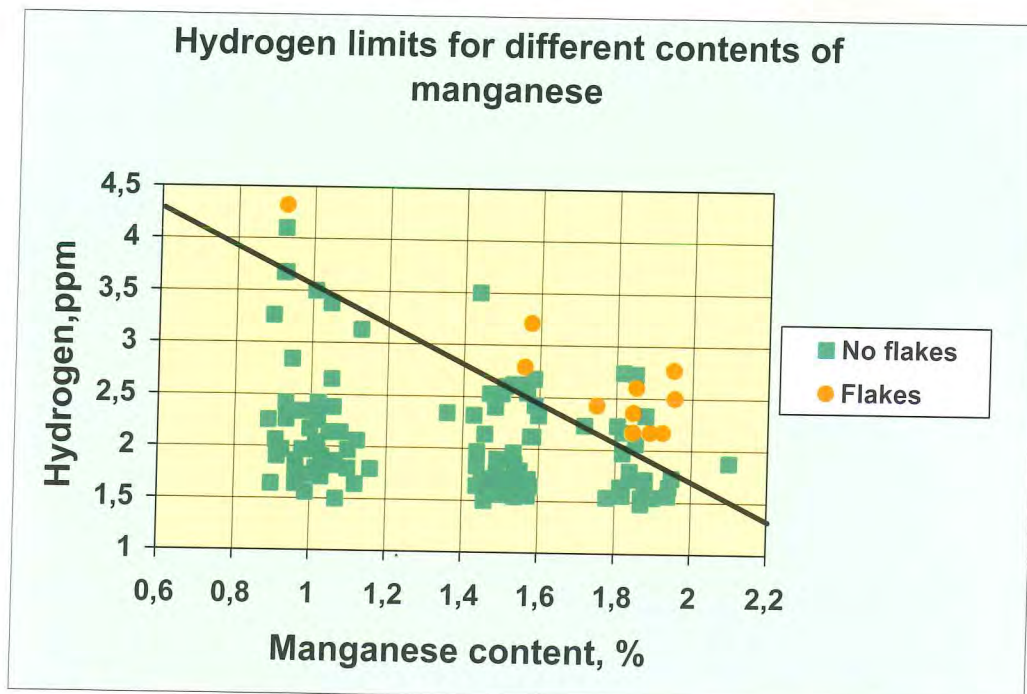
B. Hydrogen induced Cracks (HIC)

It is essential to reduce the hydrogen content as minimum steel grades used in pipelines or vessels contain sulphuric gasses. The hydrogen in these gasses will diffuse in the steel and collect itself into weak spots. If large quantities of hydrogen are already present in the steel, small amounts of diffused hydrogen are sufficient to induce cracks resulting in premature failure.

C. Fish eyes

The occurrence of fish eyes is related to the hydrogen content of the steel. Fish eyes are formed in the presence of tensile strains above the yield stress of steel. The embrittlement they cause is characterised by a decreased prolongation and is recognised by the appearance of these so-called fish eyes.

D. Blowholes and pinholes

Subsurface blowholes are a major cause of surface defects in the as-rolled product and are due to excessive amounts of dissolved gas N_2, CO and hydrogen. Increased quality specifications demand cleaner steels with reduced impurities and blowholes. Figure 34 shows the relationship between dissolved gas content and the occurrence of blowholes and pinholes.
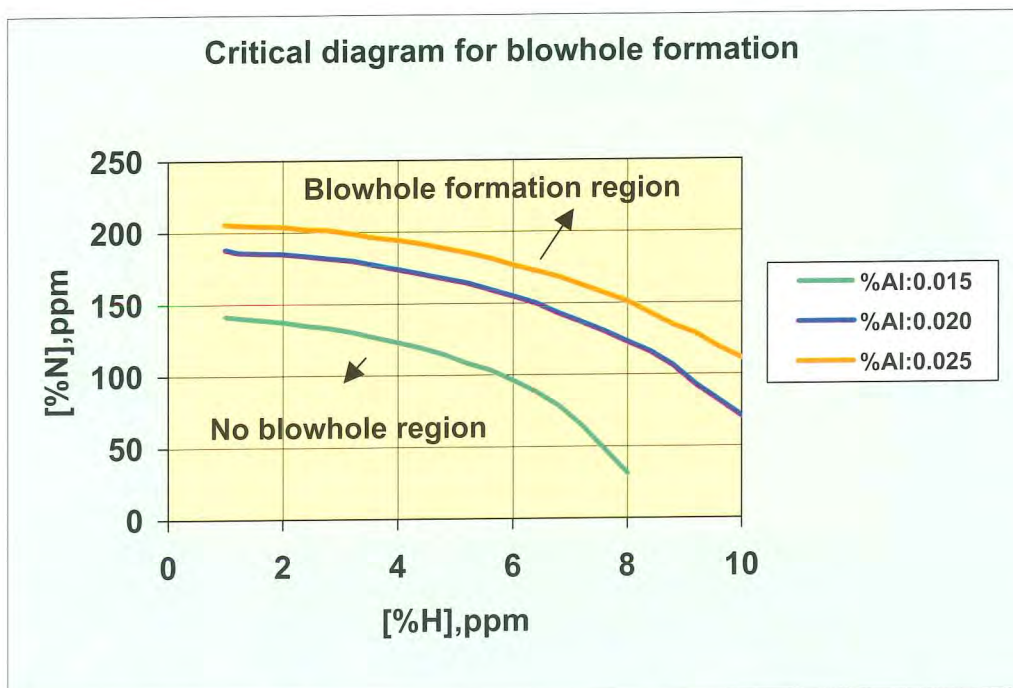
Figure 34: High hydrogen and nitrogen could result in the formation of blowholes [13]

E. Longitudinal surface cracks

The incidence of longitudinal surface cracks is increased if the hydrogen content of the steel increases.

F. Heat treatments

Additional heat treatments can be applied to decrease the hydrogen content after casting. A correct hydrogen analysis is crucial as the hydrogen content decreases slowly (figure 35). The measured hydrogen level will determine the time of treatment. Erroneous too high hydrogen analyses will result in excessive and expensive heat treatments. Too low analyses, however, will result in increased occurrence of flakes.
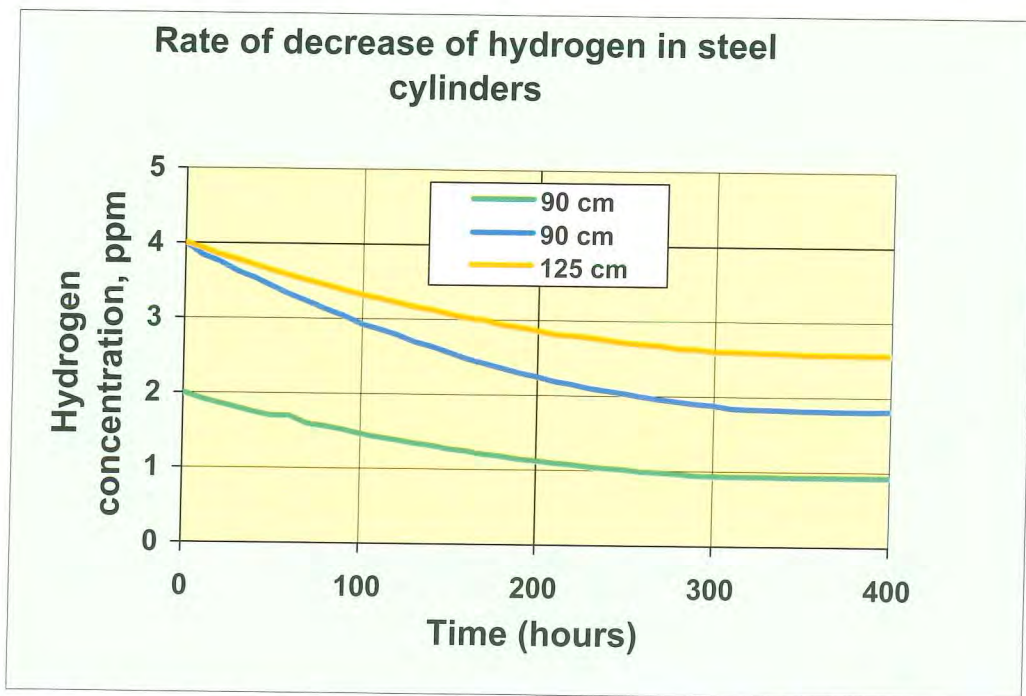
Figure 35: The slow reduction of hydrogen in large steel cylinders during additional heat treatments[a].

APPENDIX

MATHEMATICAL MODELS DEVELOPED WITH HYDRIS®

1. CALCULATION OF THE CONTRIBUTION OF ADDITIONS

Although no single model is suitable for all plants it is informative to examine a specific model. For this purpose the model developed by Mr. Varcoe and co-workers of BHP-Steel Australia is selected14.
The model describes Hydrogen pickup in the ladle prior to ladle treatment, table 1, and due to ladle treatments, table 2. The evaluation is based on Hydris®, measurements before and after the ladle treatmenttment. An initial measurement of Hydrogen is used to determine the effect of upstream practices. The final minus initial measurement is used to determine the effect of ladle treatment practices. In both cases a large number of variables were submitted to regression to establish the most influential predictors.

A. *Pre-ladle treatment*
   Table 1: Pre-treatment model
   Model r2= 0.70
   Number of data points = 99
   Standard deviation of prediction = 0.47

MODEL

VARIABLE	UNITS	COEFFICIENT	UNITS
Constant		1.82	(ppm)
Tap S	(%)	-28.69	(ppm/%)
1/Tap C	(1/%)	0.026	(ppm.%)
pH_2O (*)		35.51	(ppm)
Equilibrium Hydrogen (**)	(ppm)	0.018	(-)
(**)	(bags)	0.012	(ppm/bag)
Char addition at tap	(kg)	0.00027	(ppm/kg)
FeSi addition at tap	(kg)	0.00031	(ppm/kg)
FeCr addition at tap	(ton)	-0.018	(ppm/t)
Charged scrap	(ton)	-0.158	(ppm/t)
Charged dolomite			
FeSi addition LTP before first sample	(kg)	0.0047	(ppm/kg)

The Hydrogen pickup can be calculated as follows:
ΔH = 1,82-28,69 (%Si) + 0,026 (1/%C) / 35,51 . pH2O + 0,018. Heq+ 0,012.(bags)
   + 0,00027.(kg FeSi) + 0,00031 (kg FeCr) – 0,18 . (ton scrap) + 0,158 (ton.dolomite)
   + 0,0047 (kg FeSi)
(*) pH_2O can be calculated as follows: H_2O (sat)= -0,096 x 0,17 x ambient temperature (°C)
                                        H_2O (vap)= humidity / 100 x H2O (sat)
                                        pH_2O = H_2O (vap) / 101.3
(**) Heq (equilibrium) can be calculated as follows: $H = (\frac{1,024.10^{-7}.pH_2O}{Q/10000})^{1/2}.10.000$ *(ppm)*

B. *Pre-ladle treatment*
   Table 2: Ladle treatment model
   Model r2= 0.67
   Number of data points = 84
   Standard deviation of prediction = 0.18 ppm

MODEL

VARIABLE	UNITS	COEFFICIENT	UNITS
Constant		0.51	(ppm)
Initial S	(%)	-0.83	(ppm/%)
Initial C	(1%)	-0.37	(ppm.%)
Equilibrium Hydrogen	(ppm)	-0.0096	(-)
Dolomite addition	(kg)	0.00034	(ppm/kg)
Scrap addition	(kg)	0.00004	(ppm/kg)
Al pucks addition	(kg)	0.005	(ppm/kg)

The Hydrogen pickup can be calculated as follows:
ΔH = 0,51 – 0,83 (%S) – 0,37 (1/%C) – 0,0096.H_{eq} + 0,00034 . (kg dolomite)
   + 0,00004 (kg scrap) + 0,005 (kg Al)

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