Investigation of Hydrogen and Nitrogen Content in Compacted Graphite Iron Production

Master Thesis Project

Dimitrios Siafakas

Kungliga Tekniska Högskolan
Dept of Material Science and Engineering
2012
Contents

1. INTRODUCTION ........................................................................................................ 4
2. THEORY .................................................................................................................... 5
   2.1 Compact Graphite Iron – CGI ............................................................................ 5
   2.2 Process Control and production of CGI .......................................................... 6
   2.3 Gas Porosity in Cast iron ................................................................................. 7
   2.4 Solubility of gases in cast iron .......................................................................... 7
   2.5 Hydrogen .......................................................................................................... 8
   2.6 Nitrogen ............................................................................................................ 8
3. HYDROGEN AND NITROGEN ABSORPTION IN GREY CAST IRON ........... 8
   3.1 The influence of the melting method [4] ......................................................... 9
   3.2 The influence of the mould filling .................................................................. 10
      3.2.1 Specially designed gate system and resin binder[39] .............................. 10
      3.2.2 Traditionally designed gate system in green sand molds[4] .......... 12
4. EXPERIMENTAL PROCEDURE ........................................................................ 14
   4.1 Hydris ............................................................................................................... 15
   4.2 Spectrometer - Optical Emission Spectroscopy (OES) .................................... 18
   4.3 Combustion Analysis ....................................................................................... 18
   4.4 Samplers .......................................................................................................... 18
   4.5 Measuring Procedure ...................................................................................... 19
      4.5.1 First Experiment ....................................................................................... 19
      4.5.2 Second experiment .................................................................................. 21
      4.5.3 Third experiment ..................................................................................... 22
   4.6 Temperature distribution simulation in the feeder after mold filling ........... 22
5. RESULTS ................................................................................................................ 26
   5.1 Hydris measurements ...................................................................................... 26
   5.2 Nitrogen measurements .................................................................................. 30
6. DISCUSSION .......................................................................................................... 36
   6.1 Hydrogen ......................................................................................................... 36
      6.1.1 First Experiment ....................................................................................... 36
      6.1.2 Second Experiment .................................................................................. 37
      6.1.3 Third Experiment ..................................................................................... 37
   6.2 Nitrogen .......................................................................................................... 37
      6.2.1 First Experiment ....................................................................................... 37
6.2.2 Second Experiment

6.2.3 Third Experiment

6.2.4 Comparison between Optical Emission Spectroscopy and Combustion Analysis methods

7. CONCLUSIONS

8. ACKNOWLEDGEMENTS

9. REFERENCES
1. INTRODUCTION

This research is part of a wider program called SPOFIC which is a program performed in co-operation between Jönköping University, Kungliga Tekniska Högskolan, Volvo Powertrain AB, Scania CV AB, Arvika Gjuteri and Swerea-Swecast.

Due to higher environmental demands the heavy automotive industry needs to reduce the amount of pollution in exhaust gases. One way to do this is by increasing the combustion pressure in engines. Thought, increased combustion pressure also raises the demands for engine parts with higher mechanical properties during operation in elevated temperatures. Nowadays, due to its good thermal conductivity and vibration dumping capacity, lamellar cast iron is most commonly used for the production of engine parts but its tensile properties are close to the limit to withstand the elevated combustion pressure.

Compacted graphite iron (CGI) is a grade of cast iron with morphology between lamellar and nodular cast iron. Due to the compacted morphology of graphite in CGI’s the material has increased tensile properties compared to lamellar cast iron and better thermal conductivity compared to nodular cast iron. Some disadvantages of this grade of cast iron are the narrow production technology windows with increasing technological disciple and the increased machining expenses. Also, due to the lack of production experience defects formation such as shrinkage porosity makes it more difficult to produce cast components with adequate quality. [1]

Previous investigations have shown that shrinkage porosity cavities in complex shaped automotive components produced with CGI are protected from contact with the surrounding atmosphere during solidification [2], which indicates internal shrinkage porosity formation during solidification. Usually, heterogeneous porosity nucleation in metallic liquids are facilitated by precipitation of Hydrogen and Nitrogen in the melt [3]

Other investigations on LGI have shown that H and N content can vary but never overgrow the solubility limit in molten cast iron depending on the melting practice and indicating that the filling conditions into the casting mold could significantly contribute and push the content of H and N to the solubility limit. [4]

For comparison reasons, a literature survey regarding nitrogen and hydrogen absorption in Grey Cast Iron is presented in chapter 3.

The aim of this research is to investigate if Hydrogen and Nitrogen are present over the solubility limit in molten iron aimed for CGI production using reliable measuring equipment.
2. THEORY

2.1 Compact Graphite Iron – CGI

As already mentioned, CGI is an intermediate grade of cast iron between lamellar and nodular cast iron. The graphite particles in CGI are elongated and randomly oriented as in grey iron but are shorter and thicker with rounded edges. This kind of morphology provides improved mechanical properties compared to gray iron due to the fact that it inhibits crack initiation and growth. CGI also includes a percentage of nodular graphite particles. As the amount of those nodules increases, stiffness and strength also increase but on the other hand cast ability and thermal conductivity decrease. According to CGI production practices, a maximum of 20% nodularity of the existing graphite is allowed. Figure 1 shows a comparison between the microstructures of CGI, lamellar iron and nodular iron. 

![Figure 1 Micro-structure of LGI, CGI and NGI respectively](image1)

CGI also has higher elastic modulus and higher fatigue strength than gray iron. When CGI is used for cylinder blocks manufacturing, the higher elastic modulus results in slighter bore distortion reducing consumption and emissions. CGI has a fatigue limit of 175MPa which is almost double than the 62-79MPa limits of grey iron. Due the increased fatigue strength significantly lighter cylinder blocks can be produced. Table 1 shows the mechanical properties for some common CGI grades.

<table>
<thead>
<tr>
<th>Grade</th>
<th>UTS (MPa)</th>
<th>YS (MPa)</th>
<th>E (%)</th>
<th>HB 30 (typical results)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EN-GJV-300</td>
<td>500-375</td>
<td>220-295</td>
<td>1.5</td>
<td>140-210</td>
</tr>
<tr>
<td>EN-GJV-350</td>
<td>350-425</td>
<td>260-335</td>
<td>1.5</td>
<td>160-220</td>
</tr>
<tr>
<td>EN-GJV-400</td>
<td>400-475</td>
<td>300-375</td>
<td>1.0</td>
<td>180-240</td>
</tr>
<tr>
<td>EN-GJV-450</td>
<td>450-525</td>
<td>340-415</td>
<td>1.0</td>
<td>200-250</td>
</tr>
<tr>
<td>EN-GJV-500</td>
<td>500-575</td>
<td>380-455</td>
<td>0.5</td>
<td>220-260</td>
</tr>
</tbody>
</table>

Table 1 CGI Grades – German Standard VDG Merkblatt W50 (2002)

Additionally, CGI has comparable heat conductivity with lamellar graphite iron and much higher than nodular graphite iron.

All of the above features of CGI make it a very suitable material for the production of internal combustion engine blocks where high temperature operation strength, vibration dumping and proper heat rejection demands are high.
2.2 Process Control and production of CGI

Considering process control, Compact Graphite Iron Production has a very narrow technological window with high demands and attention to the details.

One important factor is the sulfur content of the base iron. CGI production is favored when the sulfur content is lower than 0.02%. There are two different ways to obtain low sulfur base iron.

i) Obtaining the iron directly from a cupola furnace

ii) Obtaining the iron from an electric induction furnace initial charged with low sulfur material.

In the case of the cupola furnace the initial sulfur content is around 0.1%. In order to achieve the desired content of 0.01%, desulfurization of the iron is required.

Before tapping of the melt into the ladle, the ladle is preheated up to 1520 – 1530°C by gas flame to avoid heat losses when the melt is charged from the furnace to the ladle.

At the next step which is called “first treatment”, active elements, ferromagnesium and rare earth metals which contribute to the oxygen removal or act as nodularizers are added into the ladle. All the alloying elements are covered by a buffer, called alloying pocket. This buffer delays the reaction between the hot metal and the alloying elements until all of the metal is charged. This helps to control the fading effect of magnesium and prevent wasting expensive rare earth metals \[8\].

As Mg plays a significant role in the formation of CGI by partially removing oxygen and sulfur, keeping the nodularity of CGI between 10 – 20% and avoiding the development of graphite flakes, in addition of carbon control, it is very important to carefully monitor and keep the Mg content between a very narrow window of 0,005% - 0,008%. This is possible only by a highly precise control of the second treatment of the melt. In order to evaluate the exact amount of alloying elements required for this step several commercial methods have been introduced. Some of them are based on thermal analysis of the cooling curves of the melt or measurement of the oxygen content. One example is the method developed by SinderCast. This method is based on analyzing the cooling curve of the melt and predicting the solidification behavior by simulating magnesium fading \[9\].

Regarding the optimum content of carbon and silicon for CGI the amount should be kept between 3,5%–3,8% and 1.7%-3% respectively.
2.3 Gas Porosity in Cast iron
One important factor that contributes to the total porosity in cast iron is gas evolution. It is known that the solubility limit is higher in the liquid phase than the solid phase. So, during solidification, the solute gases tend to be rejected from the solidifying phase to the remaining liquid phase. As the last remaining and supersaturated liquid continuous to solidify, gas can evolve due to the decreasing solubility limit and gas pores are generated. The gases that most commonly generate porosity in iron alloys are Hydrogen and Nitrogen. The sources of those gases can be moisture, damp refractory and the atmosphere. The gas content in the hot metal can also be increased during mould filling due to moisture on the inner surface of the mould, by the breakdown of clay limestone, magnesia or iron oxides and hydroxides or even by gases released from the degradation of organic binders. The energy required for a homogeneous nucleation of a gas bubble is very large, so usually gas nucleation takes place at shrinkage porosity sites and on other melt contaminants like oxide inclusions where the required energy for the gas nucleation is much lower (heterogeneous nucleation).

2.4 Solubility of gases in cast iron
The solubility of gases in liquid metal depends mainly on:

i) Temperature

ii) Partial pressure of the reacting gas

iii) Composition of the melt (alloying element with higher affinity to the gas than iron tend to increase the solubility limit of the gas)

The rate of absorption of gases in the liquid metal depends on the chemical reaction rate on the surface of the metal. Larger surface also means higher gas absorption. For nitrogen and hydrogen pick up one of the most important factors is the total oxygen content in the melt. Also, their solubility affects each other. High hydrogen content can make tolerable nitrogen content dangerous and the cumulative effect of both gases can results in gas defects.

2.5 Hydrogen
The main sources of hydrogen are water and organic materials. Water can be found as moisture in the raw material, humidity in the air or even as vapor in the mould. It is considered to be the main contributor of hydrogen as it reacts strongly with the molten metal. This reaction results in the dissociation of water in H₂ and O₂ and eventually in the dissolution of hydrogen into the liquid iron.

The solubility of hydrogen in pure iron at 1600 °C is around 24ppm. Though, the high content of carbon and silicon in cast iron decreases the solubility limit even
more at a value around 15ppm. The usual content in cast iron is around 2ppm. [15],[17],[18],[19]

The hydrogen solubility limit strongly depends on the temperature. It significantly increases as the temperature increases. In solid state it depends on the phase state of the iron. Solubility is higher in austenite than ferrite. [20]

2.6 Nitrogen
Atmospheric Air contains 79% nitrogen in the form of molecular Nitrogen. As molten iron is constantly in contact with the air it would be wise to consider it as the main source that contributes in the total content of Nitrogen in the melt but molecular Nitrogen is only slightly soluble in the liquid iron. On the other hand atomic nitrogen is quite soluble. Thermal breakdown of molecular nitrogen, decomposition of nitrogen containing compounds such as mould or core materials with resin binder, pig iron, foundry returns and scrap are the main sources of atomic nitrogen. [15],[21]

The solubility on nitrogen in pure iron at 1600°C is around 450ppm but in cast iron it drops to 150ppm. The usual content is around 20-80 ppm. It is known that defects due to Nitrogen could possibly appear at contents around 110-150ppm. [15],[22],[23],[24]

In contrast with Hydrogen the solubility of Nitrogen only slightly increases when temperature is increased. [20]

3. HYDROGEN AND NITROGEN ABSORPTION IN GREY CAST IRON
Two different researches titled ´´Influence of Melting Process on Gas Content in Grey Iron´´ and "Gas absorption in grey cast iron during mould filling" were performed by the Department of Mechanical Engineering of Jönköping’s University with the cooperation of several companies which also take part in the SPOFIC program. The aim of the first research was to investigate the influence of the whole melting process on the gas content of gray cast iron. Starting with the melting furnace and continuing to the holding furnaces, the ladle or tundish before pouring and finally the mold, gas measurements for oxygen, hydrogen and nitrogen were taken at every step of the production line. The aim of the second research was to investigate how Hydrogen and Nitrogen absorption during mold filling is influenced by the chemicals used for the mold production and also by the casting speed.

In this chapter the nitrogen and hydrogen measurements of both those researches will be presented for comparison reasons. The Hydris method was used for the hydrogen measurements and the optical emission spectrometry method for the nitrogen measurements.
It is noted that all the graphs were taken as they are in the original document and no alterations of any kind were made.

3.1 The influence of the melting method \[4\].

As shown in Graph 1. Hydrogen content in the melt from the induction furnaces is higher than the cupola furnace. The melt from the cupola furnace has a concentration of 1.5 ppm, while the concentrations in the induction furnaces vary from 2 to 2.5 ppm. Possible reasons for this differences are the different charge compositions and melting techniques. The cupola furnace has a significant temperature gradient from top to bottom which means that the charge material is preheated before it is totally melted and the moisture evaporates.

Regarding the nitrogen content, the research showed that the iron produced by the induction furnace had a significantly lower nitrogen content than the cupola furnace. The nitrogen content was between 75ppm and 95ppm for the induction furnaces and 105 ppm for the cupola furnace. Large amounts of steel scrap, blown air and the coke fuel used for the cupola production are probably the reasons of this higher nitrogen content.

It should be noted that the nitrogen values from the cupola furnace are very close to the 110-150ppm values reported in castings with defects.

Graph 2: Concentrations of a) hydrogen and b) nitrogen in iron from two different induction furnaces and a cupola furnace. The temperature of the melt varied between 1400 - 1450 °C \[4\].
3.2 The influence of the mould filling

3.2.1 Specially designed gate system and resin binder\cite{29}.

For the purposes of this research, a specially designed gate system was constructed and six different types of molds were used. The gate system and mold types are shown in figure 2 and table 2.

![Figure 2 Sketch of mold design](image)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Binder type</th>
<th>Content, %</th>
<th>Coating type</th>
<th>Steel plate</th>
<th>Gating system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy – reference</td>
<td>Epoxy $SO_2$</td>
<td>1:2</td>
<td>Aluminium silicate</td>
<td>Closed</td>
<td>Closed</td>
</tr>
<tr>
<td>Epoxy – permeable</td>
<td>Epoxy $SO_2$</td>
<td>1:2</td>
<td></td>
<td>Perforated</td>
<td></td>
</tr>
<tr>
<td>Epoxy – coated</td>
<td>Epoxy $SO_2$</td>
<td>1:2</td>
<td></td>
<td>Closed</td>
<td>High turbulence</td>
</tr>
<tr>
<td>Epoxy – turbulent</td>
<td>Epoxy $SO_2$</td>
<td>1:2</td>
<td></td>
<td>Closed</td>
<td>Low turbulence</td>
</tr>
<tr>
<td>Epoxy – filter</td>
<td>Epoxy $SO_2$</td>
<td>1:2</td>
<td></td>
<td>Closed</td>
<td></td>
</tr>
<tr>
<td>PUCB</td>
<td>PUCB</td>
<td>1:6</td>
<td></td>
<td>Perforated</td>
<td></td>
</tr>
<tr>
<td>Green sand</td>
<td>Green sand</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Mold formulation: content of binder is based on sand weight.
Graph 3 shows the change of hydrogen concentration during mold filling for six different types of moulds: each is the average value based on at least three measurements. A minimum increase of 0.9 ppm is observed in Epoxy-Filter mold and a maximum increase of 1.4 ppm in Epoxy - Turbulent and Epoxy - Coated molds.

Graph 4 shows the change of nitrogen concentration during mold filling for six different types of molds after recalculation. Zero change in observed for Epoxy-Filter mold and a maximum increase of 13 ppm is observed in PUCB mold.

The main outcome of this research is that the increase of Hydrogen and Nitrogen in the iron during mold filling is directly influenced by the mold filling velocity. The increased mold filling velocity creates an increasing surface turbulence between the flowing liquid and the mold atmosphere which results in larger exchange of elements between the liquid and the mold.
3.2.2 Traditionally designed gate system in green sand molds[4]

Graph 5 shows the hydrogen content measured in five different samples in the ladle or tundish before pouring and in the mold after pouring. The initial hydrogen content was around 1.8 ppm and the final content after pouring varied from 2.4 to 3.9ppm. As expected the hydrogen content increased after casting. The increase varied from 25% to 117% but the hydrogen content never passes over the solubility limit.
Graph. 5 Hydrogen concentrations in the melt before casting and in the mold. The measuring before casting was performed either in a tundish or in a ladle just before pouring into the mold. The measuring in the mould was performed in an open feeder\textsuperscript{[4]}.

Due to the low temperatures in the mold it was very difficult to obtain samples with adequate quality and only two measurements were obtained which are shown on graph 6. A small increase in the nitrogen content of around 10% was observed with the initial value approximately at 80ppm and the final value approximately at 88 to 90 ppm.
4. EXPERIMENTAL PROCEDURE

Three different experiments were conducted for the purposes of this research.

i) Hydrogen and Nitrogen content measurements, before and after casting, in a melt produced from very high quality raw material in an induction furnace intended for Compacted Graphite iron production.

ii) Hydrogen and Nitrogen content measurements, in the ladle, in three different melts. One produced from 100% dry CGI chips melted in an induction furnace, one with a traditional charge aimed for LGI production melted in a cupola furnace and one from 55% dry chips + 45% wetted chips melted in an induction furnace.

iii) Hydrogen and Nitrogen content measurements, before and after casting, in two different melts. One produced from wet SGI chips and one from nitrogen enriched, wet SGI chips. Both melts were melted in an induction furnace.

Generally, the experimental procedure follows the previous ones used in the literature.

Three different methods were used to analyze the total content of dissolved hydrogen and nitrogen in Compacted Graphite Iron (CGI).
Hydrogen content was measured online in liquid iron. The equipment used for the measurement of hydrogen is called Hydris and was provided by Heraeus Electro-Nite AB.

The nitrogen measurement was performed in solidified samples also taken in the ladle and in the mold. The analysis was done in one of the co-operating foundries labs with a commercial spectrometer suitable for iron composition analysis and also with the combustion analysis method.

4.1 Hydris

Hydris is suitable for direct online measurement of hydrogen in molten iron or steel. The measurement can be performed in the ladle, tundish or mould. The equipment consists of a processor unit (Multi-Lab Hydris), a pneumatic unit and a lance on which the disposable probes are fitted. A Nitrogen Detector (AGA, Product Number: 100 076 540) with a fitted pressure reducing valve, adjustable between 2.5 and 12 bars must also be connected to the system\(^{[25]}\). Figure 3 shows the system components and the probes.

During the measurement the nitrogen carrier gas is circulated between the melt and the pneumatic unit. The carrier gas picks up the hydrogen from the melt and then it is recollected by a porous brick in the probe for further analysis in the pneumatic
unit. The measurement stops when equilibrium is obtained between the hydrogen in the melt and the hydrogen content in the gas. The analysis of the hydrogen content is done by a thermal conductivity detector in the pneumatic unit. [24] Figures 4 and 5 show the Hydris measurement principle and the Hydris insert, respectively.
Some restrictions for Hydris are: \[^{25}\]

i) Oxygen activity must not exceed 200ppm

ii) The titanium content of the melt must not exceed 0.08%

iii) The sulfur content must not exceed 0.2%

iv) The bath temperature must not exceed 1680 °C

For each measurement the probe should be held vertical relatively to the metal surface with no more than 15° deviation in any direction from the normal of the surface. To achieve equilibrium a time of 90sec is preselected and the end of measurement is indicated by the pneumatic unit by a signal. Before measurements, it is important to perform leak test and air simulation as well as calibration of the instrument. The results are displayed on the processor unit as a graph and can be printed. \[^{25}\]

Hydris gives an accurate value of the hydrogen partial pressure which can then be converted to hydrogen content by the use of Sievert’s Law. \[^{25}\]

\[
[H] = \frac{K}{f} \sqrt{p(H_2)} (1)
\]

Sievert’s Law depends on the equilibrium between dissolved hydrogen and the partial pressure of hydrogen. The \(K/f\) factor depends on the chemical composition of the iron and on the temperature. \(K\) is the equilibrium constant which can be calculated by \[^{25}\]

\[
logK(T) = \frac{-1900}{T} + 0.9201 (2)
\]

and \(f\) is the activity coefficient of hydrogen which can be calculated by \[^{25}\]

\[
log f_i = \sum_{j=2}^{k} e_i^j [\%j] (3)
\]

Where \(e_i^j\) is the interaction coefficient between hydrogen and the alloying elements of the iron.

The \(k/f\) factor can be used as a pre-selected value in the processor unit in order to obtain some preliminary results. But for more accurate results the hydrogen content is recalculated after obtaining the exact temperatures and composition of the iron melt.
4.2 Spectrometer - Optical Emission Spectroscopy (OES)
The Nitrogen analysis was performed at the foundry’s laboratory with the help of a commercial spectrometer used for composition analysis purposes. OES main principal is based on the fact that each element when ionized emits a characteristic electromagnetic wave. In the machine, plasma is generated, usually from Argon Gas, a spark hits the sample and the atoms on the surface are ionized. The electromagnetic wave emitted from those atoms is detected by a sensor in the system and then it is analyzed. The intensity of each distinctive wavelength is used to calculate the total content of its elements. The main principals of the OES method are shown in figure 6. \[^{[26]}\]

![Figure 6 Main principal of the OES method][27]

The spectrometer used was an OE spectrometer ARL 3460, with channels for C, Si, Mn, P, S, Cr, Ni, Mo, Cu, Sn, Pb, Al, Ti, V, W, B, Nb, Zr, Co. An average composition for each element is calculated by the software (WinOE) after three sparks on each sample. Different reference material is used to control differences in composition. For example, carbon content.

4.3 Combustion Analysis
The second method used for the nitrogen analysis was combustion analysis. Combustion analysis is a method used in both organic and analytical chemistry to measure composition. A sample is combusted in an oven and the resulting combustion products can be quantitatively analyzed \[^{[28]}\]. A Leco TN-114 equipment was used for this method. A certain amount of a grinded sample is put inside an oven connected to the analyzing instrument. Also here reference material is used to control differences in carbon and sulfur content.

4.4 Samplers
For the Nitrogen measurements two different samples were needed, disks for the spectrometer’s analysis and pins for combustion analysis. Samplers SaF400P6 provided by Heraeous Electro-nite AB were used. The SaF400P6 samplers are made from resin bonded sand. A test disk and two test pins are obtained. The disks have a diameter of 35mm and 4mm thickness. One of the pins has 6mm diameter and a length of 42mm and the other has the same length but differs in diameter, 5mm at
one end and 4mm in the other. Chills in the sampler promote the rapid solidification of the disks. The samplers are introduced into the melt with the help of a lance, filled in a few seconds and left to solidify in room temperature \[3\]. Figure 7 shows the SaF400P6 sampler.

![The SaF400P6 sampler.](image)

4.5 Measuring Procedure

The experiments have been performed in one of the co-operating companies foundry.

4.5.1 First Experiment

The iron was transferred from one of the foundry’s induction furnaces to a ladle. Then the ladle was transferred to a wire feeder to add the inoculants and to be treated with aFeSiMg based additions accordingly for CGI production. Samples, temperature and hydrogen measurements were taken in the ladle after the treatment and in the mold immediately after casting. Four engine block molds were casted and the procedure was repeated for each one of them. During the casting of the third mold an extra measurement was taken in the ladle before the treatment procedure. The scope of this extra measurement was to find if the treatment procedure somehow influences the Hydrogen and Nitrogen content of CGI.

For the experiment’s purposes, each mold was specially designed to have an open feeder of 25cm depth and 15cm diameter. The feeder was opened before the mould filling, placed in the mould in such a way that it could collect the molten metal after it came in contact with the mould components and create a pool of metal for the hydris measurment. A 3D/CAD model of the mould and the feeder opening
procedure are shown in figures 8 and 9. The yellow surface shows the position of the feeder where the metal enters the mold and the purple surface indicates the feeder where the metal is collected at the end of the mold filling.

![Figure 8 Inner and outer 3D/CAD models of the mould including the specially designed feeder for the hydri measurement (Provided by Volvo Powertrain AB)](image)

![Figure 9 The feeder opening procedure.](image)

A schematic for the measuring procedure for each mold is shown in figure 10.
The purpose of the experiment was to investigate the changes of Hydrogen and Nitrogen content in the melt due to the mold filling and also due to the inoculation process. Furthermore it was interesting to see if there was shrinkage porosity found in the castings.

### 4.5.2 Second experiment

For the second experiment the melts came from three different sources.

i) 100% dry CGI chips melted in an induction furnace.

ii) traditional charge melted in a cupola furnace.

iii) 55% dry + 45% wetted CGI chips melted in an induction furnace.

The melt was transferred from the holding furnace to a ladle. For each of the three ladles, several hydrogen measurements and samples were taken in time intervals of around 12 minutes and until the melt temperature had dropped at 1300°C.

The purpose of this experiment was to investigate how the temperature, the melting furnace technology and the raw material quality influences the hydrogen and the nitrogen content of the iron melt before casting.
4.5.3 Third experiment
The experimental procedure for the third experiment was exactly the same as in the first experiment with a difference only in the raw material used for the production of the melt. Four trials were made. The raw materials were selected from less pure compositions which could possibly be used in case of missing high purity raw material and high production rates.

For the first two molds the melt was produced from wetted SGI chips and for the last two molds the raw material was nitrogen enriched wetted SGI chips.

The purpose of this experiment was to investigate how the raw material influences the hydrogen and nitrogen content of CGI before and after casting and also determine if the increased nitrogen content can influence the formation of shrinkage porosity in the final casting.

4.6 Temperature distribution simulation in the feeder after mold filling.
For the case of hydrogen content after mold filling the experimental temperatures of the melt in the feeder measured after the Hydris procedure cannot be considered accurate because they are very close to the liquidus temperature. However the Hydris measurement needs a separate temperature measurement to recalculate the H content as a function of the chemical composition and the temperature. The input
average temperature for the recalculation has been simulated using a 3D thermal simulation cycle.

An initial simulation was performed for the mould filling in order to obtain more accurate temperatures in the feeder just before introducing the Hydris probe in it. The initial temperature chosen for this part of the simulation was 1400°C which is a mean value of the temperatures measured during the experiment just before the mold filling of all molds. For the second part of the simulation a geometry with the same dimensions and identical properties with the Hydris probe was introduced in the model. The simulation was run for a period of 1 minute and 30 seconds which corresponds to the average time needed for a Hydris measurement.

Figures 12 to 15 show four snapshots of the second part of the simulation at 30s, 49s, 65s and 77s respectively. The figures represent the temperature distribution into the mold, the feeder and the probe. The average temperature of the melt during the hydris measurement around the probe was 1300°C. The highest value was 1330°C at 30s and the lowest 1245°C at 77s.
Figure. 13 Magmasoft simulation snapshot at 49s

Figure. 14 Magmasoft simulation snapshot at 65s
Figure. 15 Magmasoft simulation snapshot at 77s
5. RESULTS

5.1 Hydris measurements

Table 3 shows the results from the Hydris measurements of the first experiment.

<table>
<thead>
<tr>
<th>Casting No</th>
<th>Ladle Before Treatment</th>
<th>Ladle After Treatment</th>
<th>Mould</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Temperature</td>
<td>1381</td>
<td>1180</td>
<td>1300</td>
</tr>
<tr>
<td></td>
<td>PH2</td>
<td>11,68</td>
<td>19,53</td>
<td>19,53</td>
</tr>
<tr>
<td></td>
<td>k/f</td>
<td>0,319</td>
<td>0,22</td>
<td>0,277</td>
</tr>
<tr>
<td></td>
<td>ppm Calculated</td>
<td>1,09</td>
<td>0,97</td>
<td>1,22</td>
</tr>
<tr>
<td></td>
<td>ppm Hydris (k/f=425)</td>
<td>1,5</td>
<td>1,9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Time</td>
<td>09:42:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Temperature</td>
<td>1408</td>
<td>1200</td>
<td>1300</td>
</tr>
<tr>
<td></td>
<td>PH2</td>
<td>8,86</td>
<td>59,51</td>
<td>59,51</td>
</tr>
<tr>
<td></td>
<td>k/f</td>
<td>0,331</td>
<td>0,229</td>
<td>0,276</td>
</tr>
<tr>
<td></td>
<td>ppm Calculated</td>
<td>0,98</td>
<td>1,76</td>
<td>2,13</td>
</tr>
<tr>
<td></td>
<td>ppm Hydris (k/f=425)</td>
<td>1,3</td>
<td>3,1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Time</td>
<td>10:58:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Temperature</td>
<td>1431</td>
<td>1385</td>
<td>1184</td>
</tr>
<tr>
<td></td>
<td>PH2</td>
<td>7,12</td>
<td>8,11</td>
<td>65,4</td>
</tr>
<tr>
<td></td>
<td>k/f</td>
<td>0,343</td>
<td>0,319</td>
<td>0,222</td>
</tr>
<tr>
<td></td>
<td>ppm Calculated</td>
<td>0,915238155</td>
<td>0,91</td>
<td>1,79</td>
</tr>
<tr>
<td></td>
<td>ppm Hydris (k/f=425)</td>
<td>1,1</td>
<td>1,2</td>
<td>3,2</td>
</tr>
<tr>
<td></td>
<td>Time</td>
<td>13:01:00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Temperature</td>
<td>1398</td>
<td>1181</td>
<td>1300</td>
</tr>
<tr>
<td></td>
<td>PH2</td>
<td>8,74</td>
<td>59,6</td>
<td>59,6</td>
</tr>
<tr>
<td></td>
<td>k/f</td>
<td>0,326</td>
<td>0,221</td>
<td>0,277</td>
</tr>
<tr>
<td></td>
<td>ppm Calculated</td>
<td>0,96</td>
<td>1,70</td>
<td>2,14</td>
</tr>
<tr>
<td></td>
<td>ppm Hydris (k/f=425)</td>
<td>1,3</td>
<td>3,3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Time</td>
<td>14:11:00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Hydris measurement results from the first experiment

The mold measurement for mold number 3 was not finished due to hydris equipment measurement duration limitations. Though, the partial pressure of hydrogen seemed to stabilize around 65.4 and it is considered safe to use this value to calculate the final hydrogen content.

As the simulation temperatures are much close to real life condition and there is no other way to measure the temperature during the hydris measurement the calculations using the simulation temperature are considered to be more accurate and will be used as reference.

Graph 7 shows a comparison of hydrogen content between the three different steps.
Table 4 shows the results from the hydris measurements for the second experiment.

### LADLE 1 - INDUCTION FURNACE (55% dry chips + 45% wet chips)

<table>
<thead>
<tr>
<th>Measurement No</th>
<th>Partial Pressure of H2 (k/f=0.75)</th>
<th>Hydris ppm measurement</th>
<th>Temperature</th>
<th>Time Interval (min)</th>
<th>k/f</th>
<th>[H] ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.31</td>
<td>2.6</td>
<td>1505</td>
<td>0</td>
<td>0.414</td>
<td>1.453</td>
</tr>
<tr>
<td>2</td>
<td>12.69</td>
<td>2.7</td>
<td>1479</td>
<td>9</td>
<td>0.399</td>
<td>1.421</td>
</tr>
<tr>
<td>3</td>
<td>14.44</td>
<td>2.8</td>
<td>1460</td>
<td>5</td>
<td>0.388</td>
<td>1.474</td>
</tr>
<tr>
<td>4</td>
<td>15.32</td>
<td>2.9</td>
<td>1426</td>
<td>10</td>
<td>0.369</td>
<td>1.444</td>
</tr>
<tr>
<td>5</td>
<td>17.54</td>
<td>3.1</td>
<td>1380</td>
<td>16</td>
<td>0.343</td>
<td>1.437</td>
</tr>
<tr>
<td>6</td>
<td>18.37</td>
<td>3.2</td>
<td>1338</td>
<td>16</td>
<td>0.32</td>
<td>1.372</td>
</tr>
<tr>
<td>7</td>
<td>20.71</td>
<td>3.4</td>
<td>1305</td>
<td>15</td>
<td>0.303</td>
<td>1.379</td>
</tr>
</tbody>
</table>

### LADLE 2 - CUPOLA FURNACE

<table>
<thead>
<tr>
<th>Measurement No</th>
<th>Partial Pressure of H2 (k/f=0.75)</th>
<th>Hydris ppm measurement</th>
<th>Temperature</th>
<th>Time Interval (min)</th>
<th>k/f</th>
<th>[H] ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.04</td>
<td>2.1</td>
<td>1458</td>
<td>0</td>
<td>0.388</td>
<td>1.100</td>
</tr>
<tr>
<td>2</td>
<td>9.94</td>
<td>2.4</td>
<td>1420</td>
<td>12</td>
<td>0.361</td>
<td>1.138</td>
</tr>
<tr>
<td>3</td>
<td>11.72</td>
<td>2.6</td>
<td>1387</td>
<td>14</td>
<td>0.343</td>
<td>1.174</td>
</tr>
<tr>
<td>4</td>
<td>12.01</td>
<td>2.6</td>
<td>1346</td>
<td>15</td>
<td>0.321</td>
<td>1.112</td>
</tr>
<tr>
<td>5</td>
<td>13.04</td>
<td>2.7</td>
<td>1322</td>
<td>12</td>
<td>0.308</td>
<td>1.112</td>
</tr>
<tr>
<td>6</td>
<td>14.09</td>
<td>2.8</td>
<td>1291</td>
<td>13</td>
<td>0.292</td>
<td>1.096</td>
</tr>
</tbody>
</table>

### LADLE 3 - INDUCTION FURNACE (100% dry chips)

<table>
<thead>
<tr>
<th>Measurement No</th>
<th>Partial Pressure of H2 (k/f=0.75)</th>
<th>Hydris ppm measurement</th>
<th>Temperature</th>
<th>Time Interval (min)</th>
<th>k/f</th>
<th>[H] ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.87</td>
<td>2.7</td>
<td>1499</td>
<td>0</td>
<td>0.418</td>
<td>1.500</td>
</tr>
<tr>
<td>2</td>
<td>14.95</td>
<td>2.9</td>
<td>1440</td>
<td>16</td>
<td>0.384</td>
<td>1.485</td>
</tr>
<tr>
<td>3</td>
<td>16.99</td>
<td>3.1</td>
<td>1393</td>
<td>18</td>
<td>0.357</td>
<td>1.472</td>
</tr>
<tr>
<td>4</td>
<td>19.94</td>
<td>3.3</td>
<td>1351</td>
<td>16</td>
<td>0.334</td>
<td>1.491</td>
</tr>
<tr>
<td>5</td>
<td>21.24</td>
<td>3.5</td>
<td>1317</td>
<td>16</td>
<td>0.315</td>
<td>1.452</td>
</tr>
<tr>
<td>6</td>
<td>20.25</td>
<td>3.4</td>
<td>1294</td>
<td>12</td>
<td>0.303</td>
<td>1.364</td>
</tr>
</tbody>
</table>

Table 4 Hydris measurement results from the second experiment
Graph 8 show the temperature dependence of the hydrogen content for the three different raw material qualities.

![Graph 8: Hydrogen content against temperature for three different raw material qualities.](image)

Graph. 8 Hydrogen content against temperature for three different raw material qualities.

Table 5 shows the results from the hydris measurements for the third experiment.

<table>
<thead>
<tr>
<th>Casting No</th>
<th>Ladle Before Treatment</th>
<th>Mould</th>
<th>Simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Humid SGI chips</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Temperature</td>
<td>1429</td>
<td>1196</td>
</tr>
<tr>
<td></td>
<td>PH2</td>
<td>8.06</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>k/f</td>
<td>0.343</td>
<td>0.227</td>
</tr>
<tr>
<td></td>
<td>ppm Calculated</td>
<td>0.97</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>ppm Hydris (k/f=300)</td>
<td>0.9</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>Time</td>
<td>11:42:00</td>
<td>11:54:00</td>
</tr>
<tr>
<td>2</td>
<td>Temperature</td>
<td>1440</td>
<td>1190</td>
</tr>
<tr>
<td></td>
<td>PH2</td>
<td>6.25</td>
<td>12.42</td>
</tr>
<tr>
<td></td>
<td>k/f</td>
<td>0.348</td>
<td>0.224</td>
</tr>
<tr>
<td></td>
<td>ppm Calculated</td>
<td>0.87</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>ppm Hydris (k/f=300)</td>
<td>0.7</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>Time</td>
<td>12:38:00</td>
<td>12:42:00</td>
</tr>
<tr>
<td>3</td>
<td>Temperature</td>
<td>1453</td>
<td>1211</td>
</tr>
<tr>
<td></td>
<td>PH2</td>
<td>10.68</td>
<td>33.51</td>
</tr>
<tr>
<td></td>
<td>k/f</td>
<td>0.351</td>
<td>0.234</td>
</tr>
<tr>
<td></td>
<td>ppm Calculated</td>
<td>1.15</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>ppm Hydris (k/f=300)</td>
<td>1</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>Time</td>
<td>15:27:00</td>
<td>15:34</td>
</tr>
<tr>
<td>4</td>
<td>Temperature</td>
<td>1454</td>
<td>1228</td>
</tr>
<tr>
<td></td>
<td>PH2</td>
<td>8.28</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>k/f</td>
<td>0.352</td>
<td>0.241</td>
</tr>
<tr>
<td></td>
<td>ppm Calculated</td>
<td>1.01</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>ppm Hydris (k/f=300)</td>
<td>0.9</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td>Time</td>
<td>15:54:00</td>
<td>16:03:00</td>
</tr>
</tbody>
</table>

Table 5 Hydris measurement results from the third experiment.
The measuring procedure in the mold for molds 1 and 4 was aborted by the hydris equipment with a warning message of "low vacuum pressure" which according to the hydris manual could be due to:

i) Slag

ii) Immersion angle of the probe

iii) Hardware problem

iv) Titanium or sulfur content more than 0.1%

v) Oxygen content more than 150ppm

Graph 9 shows the mean hydrogen content of the melt for Humid and Nitrogen enriched humid SGI chips in the ladle and in the mold.

![Graph 9: Hydrogen content for humid and humid nitrogen enriched SGI chips in the ladle and in the mold.](image-url)

Graph 9 Hydrogen content for humid and humid nitrogen enriched SGI chips in the ladle and in the mold.
Graph. 10 is a comparison of the mean hydrogen content of the melt from all the raw material qualities in the ladle before treatment.

![Graph 10: Hydrogen content of all raw material qualities in the ladle.]

5.2 Nitrogen measurements

Table 6 shows the nitrogen content measured with both spectrometer and combustion analysis methods for the first experiment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N(s) ppm</th>
<th>N(c) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1- A</td>
<td>61</td>
<td>56</td>
</tr>
<tr>
<td>1- B</td>
<td>59</td>
<td>50</td>
</tr>
<tr>
<td>2- A</td>
<td>62</td>
<td>51</td>
</tr>
<tr>
<td>2- B</td>
<td>58</td>
<td>51</td>
</tr>
<tr>
<td>3.1 A</td>
<td>62</td>
<td>54</td>
</tr>
<tr>
<td>3.2 A</td>
<td>64</td>
<td>55</td>
</tr>
<tr>
<td>3- B</td>
<td>66</td>
<td>57</td>
</tr>
<tr>
<td>4- A</td>
<td>71</td>
<td>56</td>
</tr>
<tr>
<td>4- B</td>
<td>67</td>
<td>56</td>
</tr>
</tbody>
</table>

1-Before treatment
2- After
A: in ladle
B: in mould

\( (s) = \text{emission spectrometry} \)
\( (c) = \text{combustion analysis} \)

Table 6 Total nitrogen content
Graphs 11 and 12 are a comparison between the three steps for both methods respectively.

Graph. 11 Comparison between three steps for the spectrometer method

Graph. 12 Comparison between three steps for the combustion analysis method

Graph. 13 is a comparison between the two different analysis methods.
Graph. 13 Comparison between Spectrometer analysis and combustion analysis methods

Table 7 shows the nitrogen measurements from the second experiment with both spectrometer and combustion analysis methods.

<table>
<thead>
<tr>
<th>Measurement No</th>
<th>Partial Pressure of H2</th>
<th>Temperature</th>
<th>Time Interval (min)</th>
<th>[N] ppm (spectro)</th>
<th>[N] ppm (combustion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.31</td>
<td>1505</td>
<td>0</td>
<td>87</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>12.69</td>
<td>1479</td>
<td>9</td>
<td>83</td>
<td>64</td>
</tr>
<tr>
<td>3</td>
<td>14.44</td>
<td>1460</td>
<td>5</td>
<td>91</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>15.32</td>
<td>1426</td>
<td>10</td>
<td>91</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>17.54</td>
<td>1380</td>
<td>16</td>
<td>96</td>
<td>59</td>
</tr>
<tr>
<td>6</td>
<td>18.37</td>
<td>1338</td>
<td>16</td>
<td>86</td>
<td>61</td>
</tr>
<tr>
<td>7</td>
<td>20.71</td>
<td>1305</td>
<td>15</td>
<td>91</td>
<td>62</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Measurement No</th>
<th>Partial Pressure of H2</th>
<th>Temperature</th>
<th>Time Interval (min)</th>
<th>[N] ppm (spectro)</th>
<th>[N] ppm (combustion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.04</td>
<td>1458</td>
<td>0</td>
<td>138</td>
<td>103</td>
</tr>
<tr>
<td>2</td>
<td>9.94</td>
<td>1420</td>
<td>12</td>
<td>130</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>11.72</td>
<td>1387</td>
<td>14</td>
<td>133</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>12.01</td>
<td>1346</td>
<td>15</td>
<td>132</td>
<td>107</td>
</tr>
<tr>
<td>5</td>
<td>13.04</td>
<td>1322</td>
<td>12</td>
<td>129</td>
<td>102</td>
</tr>
<tr>
<td>6</td>
<td>14.09</td>
<td>1291</td>
<td>13</td>
<td>131</td>
<td>102</td>
</tr>
</tbody>
</table>

Table 7 Nitrogen measurements from the second experiment
Graphs 14 and 15 show the nitrogen content of three different raw material qualities against temperature with from both analysis methods respectively.

Graph 14 Nitrogen content against temperature (spectrometer analysis method)

Graph 15 Nitrogen content against temperature (Combustion analysis method)
Table 8 shows the nitrogen measurements for the third experiment with both spectrometer and combustion analysis methods.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N(s)</th>
<th>N(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>100</td>
<td>77</td>
</tr>
<tr>
<td>1.2</td>
<td>109</td>
<td>57</td>
</tr>
<tr>
<td>2.1</td>
<td>106</td>
<td>69</td>
</tr>
<tr>
<td>2.2</td>
<td>112</td>
<td>63</td>
</tr>
<tr>
<td>3.1</td>
<td>135</td>
<td>87</td>
</tr>
<tr>
<td>3.2</td>
<td>146</td>
<td>84</td>
</tr>
<tr>
<td>4.1</td>
<td>122</td>
<td>84</td>
</tr>
<tr>
<td>4.2</td>
<td>141</td>
<td>82</td>
</tr>
</tbody>
</table>

1-in ladle (s) = emission spectrometry
2-in mould (c) = combustion analysis

Table. 8 Nitrogen measurements from spectrometer and combustion analysis methods for the third experiment.

Graphs 16 and 17 show the nitrogen content in the ladle and in the mold against the raw material quality from both spectrometer and combustion analysis methods respectively.

Graph. 16 Nitrogen content in ladle and mold against raw material quality (spectrometer analysis)
Graph 17. Nitrogen content in ladle and mold against raw material quality (combustion analysis)

Graphs 18 and 19 are a comparison of the mean nitrogen content in the ladle between different material qualities from both spectrometer and combustion analysis methods respectively.
Graph 19. Nitrogen content in the ladle against different raw material qualities (combustion analysis)

6. DISCUSSION

6.1 Hydrogen

6.1.1 First Experiment
As shown in table 3 and graph 7, the initial hydrogen content is approximately the same for the four different ladles with an average value of 0,98ppm. After pouring, an increase in the total hydrogen content is observed for all molds. This is expected due to the fact that when the melt passes over the mould walls, it captures moisture from the sand. Some amount of hydrogen could also be introduced in the melt by the combustion of the resin binders used for the cores.

For molds 2, 3 and 4 the increase seems to be stable with an average of 1,2ppm (120%). In mold 1 the increase is much lower, around 0,13ppm (13%). This could probably have happened due to a much dryer mold or some abnormality with the hydris measurement. It is important to state that because the measurement is done in an open feeder where the melt is a good mixture of the initially poured melt and the last melt poured into the mold the calculated content is actually an average for the whole melt. There is a possibility that the total hydrogen content is locally higher.
The measurement before the treatment procedure in mold 3 shows no change in the hydrogen content and indicates that the inoculation process does not affect the total hydrogen content of the melt.

6.1.2 Second Experiment
As shown in graph 8 the hydrogen content seems to be independent of the temperature changes. The hydrogen content in melt from the induction furnace with 55% dry chips and 45% wetted chips is around 1.4 ppm for all temperatures, from the induction furnace with 100% dry chips is around 1.5 ppm and for the cupola furnace around 1.1 ppm.

As expected the hydrogen content in the iron from the cupola furnace is 27% lower than that from the induction furnaces. On the other hand, although it was expected that the hydrogen content in the iron produced by the 45% wetted chips would be higher than the content in the iron from 100% dry chips, it was measured almost the same in both cases. The reason for this paradox could be that the composition was compromised by the high waiting time of the first melt in the furnace before the measurements took place.

Generally, the measurements agree well with the results taken from the prior research regarding LGI.

6.1.3 Third Experiment
As shown in graph 9. The hydrogen content for the humid SGI chips was measured around 0.9 ppm in the ladle and around 1 ppm in the mould. For the nitrogen enriched humid SGI chips was measured around 1.07 ppm in the ladle and 1.6 ppm in the mould. Again, as in the first experiment, a smaller but significant increase of 11% to 38% after pouring is observed in both cases but the solubility limit is never exceeded.

A shown in Graph 10. The lower hydrogen content in the ladle before treatment is observed in the iron produced from very high quality raw material and the higher hydrogen content in the iron produced in the induction furnace from lower quality raw material.

6.2 Nitrogen

6.2.1 First Experiment
As shown in table 6 and Graphs 11 and 12 the nitrogen content stays almost constant for all molds with an average value of 63 ppm for the optical emission spectroscopy method and 54 ppm for the combustion analysis method. This is an indication that neither the treatment process nor the pouring process affects the total content of nitrogen in the melt which means that the nitrogen absorption from the atmospheric air or from the mold substances is insignificant.
Thought, the nitrogen measurements in grey cast iron are very few and no certain conclusions are safe to be made, the composition changes in that case also seem to be very small. The initial nitrogen content in grey cast iron is also increased as hydrogen was, possibly for the same reasons. Again in both cases the nitrogen content never exceeds the solubility limit.

6.2.2 Second Experiment
As shown in graphs 14 and 15. The nitrogen content measured with the spectrometer and combustion method respectively are 90 ppm and 65 ppm in both cases of the induction furnace and 130 and 100 ppm in the case of the cupola furnace. As expected and in full agreement with the previous research for LGI the nitrogen content in the iron from the cupola melt is significantly higher.

6.2.3 Third Experiment
As shown in graph 16. The nitrogen content in the iron produced by humid SGI chips, according to the spectrometer analysis, was around 103 ppm in the ladle and 110 ppm in the mould. For the nitrogen enriched humid SGI chips the content was 128 ppm in the ladle and 143 ppm in the mould. In this case in contrast to the first experiment a small increase in the nitrogen content is observed after pouring. In both cases the nitrogen content is very close to the 110-150 ppm range where the castings tend to develop gas related defects.

Graph 18 is a comparison on the nitrogen content between different melting processes and raw material qualities based on the spectrometer analysis method. The highest nitrogen content is observed in the iron produced in the cupola furnace and the lowest in the iron from the high quality raw material.

6.2.4 Comparison between Optical Emission Spectroscopy and Combustion Analysis methods
Considering that both the samples used for each method were taken by the same SaF400P6 sample it is expected that both methods would give the same results. Though, as shown in Graph 13 and also supported by the results in tables 7 and 8, the spectrometer method gives higher measurements than the combustion method. It is clear that this difference is small in low Nitrogen contents and increases as the total Nitrogen content increases. In higher Nitrogen levels the combustion method measurements seem to lack consistency which is an indication that the method should not be considered accurate.
7. CONCLUSIONS

The conclusions of this research can be summarized to the following:

i) The total hydrogen content in CGI increases significantly after pouring of the melt into the mould.

ii) The total nitrogen content in CGI slightly increased by the casting process.

iii) Neither hydrogen nor nitrogen content seems to be affected by the treatment procedure.

iv) In the case of casting LGI blocks, Hydrogen and Nitrogen content comes close to the solubility limit which is dependent on the less clean charge material aimed for LGI. There is higher Hydrogen level after melting LGI than CGI and the content increases proportionally in both cases.

v) From the previous measurements presented in chapter 3 it is clear that besides the filling velocity, the increase of Hydrogen and Nitrogen is furthermore dependent on the atmospheric pressure in the mold cavity in the vicinity of the liquid metal and gaseous surface. The differences Hydrogen and Nitrogen content obtained in this experiment could be dependent on the differences in the manual pouring and the different time used from creating a mold to the final pouring. Different waiting time could cause different humidity level in the green sand mold depending on the time necessary to drill and prepare the mold for casting.

vi) The final Hydrogen content was lower in the case of CGI than LGI. This is comparable with the defect frequency in the foundry when comparing defects related to gas content.

vii) The nitrogen content is higher in irons produced in cupola furnaces and lower in iron produced in induction furnaces.

viii) The hydrogen content is lower in iron produced in cupola furnaces and higher in iron produced in induction furnaces.

ix) Though high quality raw material is preferable for the production of CGI, other sources of raw material could be usable as long as the nitrogen content is kept at acceptable levels.

x) The spectrometer analysis method seems to be more accurate than the combustion analysis method when measuring Nitrogen content in iron.
The cylinder blocks casted during experiments 1 and 3 were cut in critical surfaces of the solidified areas to investigate if shrinkage porosity is present. The results show no shrinkage porosity for the first experiment but shrinkage porosity is present in the third experiment as shown in figure 16.

![Shrinkage porosity in the metallic matrix of the castings from the third experiment.](image)

Figure 16. Shrinkage porosity in the metallic matrix of the castings from the third experiment.

The characteristics and the type of the shrinkage porosity were defined accurately in a previous research\cite{2}. The shrinkage porosity appears in areas known for inducing porosity. The porosity is included in the metallic matrix without any contact with the surrounding atmosphere and medium distribution. The scope of the present investigation in not to investigate the mechanism of shrinkage porosity while it has to be investigated in a future work if the shrinkage porosity found in the matrix is influenced by the Nitrogen content whet it very close to the solubility limit.

It has been evident that shrinkage porosity is formed when a less pure charge material is used. The increase of the Nitrogen is evident even by measurement but it is not so in the case of Hydrogen. In a future investigation it has to be clarified whether the increased content of solved Nitrogen or the presence of humid raw material contributes to the increased tendency of shrinkage formation by influencing the nucleation and crystal growth or whether it is influenced only by segregation of the element and diffusion to the porous region contributing to the hole growth.
8. ACKNOWLEDGEMENTS
The author of this report would like to acknowledge Jönköping University, Kungliga Tekniska Högskolan, Volvo Powertrain AB, Scania CV AB, Arvika Gjuteri and swerea-sweekcast for their participation and contribution to the SPOFIC program and also thank Professors Attila Dioszegi, Hasse Fredriksson, Pär Jönsson, PhD candidate Sadaf Vazehrad and all the participating personnel from the foundry that the experiment was performed for their unreserved help. The author would also like to acknowledge Heraeus ElectroNite AB for their help and support with the measuring equipment.
9. REFERENCES


[5] http://www.zeiss.de/c12567be0045acf1/Contents-Frame/0a8a19e66dd627b4c12574de00320026


[27] A. V. Karasev, Process control of ladle – Methods to determine inclusion characteristics, Stockholm 2011
