

Hydrogen and Nitrogen Control in Steelmaking at U. S. Steel

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Abstract

The field of steelmaking has seen an increased demand in reducing and controlling the amounts of dissolved gases in steel. Hydrogen and nitrogen are two of the most important gases which, when dissolved in liquid steel, affect its properties significantly. Both of these gases can enter the liquid steel either through steelmaking additions or by reaction of the liquid metal with the atmospheric elements. At United States Steel Corporation (U. S. Steel), empirical evidence has shown that hydrated scrap, lime and coke additions are major contributors to hydrogen pickup in liquid steel. Similarly, nitrogen impurities in ferroalloys, coke and scrap are identified sources of nitrogen. In addition, the presence of measurable traces of nitrogen in oxygen gas used at the BOP and Q-BOP has also resulted in elevated levels of nitrogen pickup. There is also an increased likelihood of higher hydrogen and nitrogen in liquid steel from overblow and reblow situations. This additional pickup of hydrogen and nitrogen gases in steel will not only affect the properties of steel; there is also significant potential for hydrogen-induced sticker breakouts to occur at the continuous caster, which could result in significant maintenance costs and productivity losses. Therefore, it is imperative to accurately quantify the amounts of hydrogen and nitrogen in liquid steel. Online hydrogen measurement uses measured hydrogen partial pressure in collaboration with equilibrium constants and interaction coefficients relevant for the hydrogen dissolution reaction. To ensure accurate hydrogen readings from the instrument, those thermodynamic values were reviewed, considering the changes in chemistry and temperature in the steel-making processes. Similarly, precautions dealing with sample preparation to ensure accurate and reproducible nitrogen measurements using optical spectrometric techniques are identified. Discussions on the potential hydrogen-induced breakouts, when uncontrolled and significantly high levels of hydrogen are present in the liquid steel, are also provided in this paper.

Introduction

Hydrogen and nitrogen are inevitable components in all commercial steels. While the presence of hydrogen provides no potential benefits, nitrogen can be considered an impurity or a desired alloying addition. Both

Hydrogen and nitrogen are two gases that, when dissolved in liquid steel, affect its properties significantly. Accurate measurement of these gases is the first step in controlling the properties of steel and preventing hydrogen-induced sticker breakouts at the continuous caster.

hydrogen and nitrogen are present interstitially in steel. Nitrogen can also be present as a nitride with aluminum, titanium and/or other nitride-forming elements, but hydrogen cannot form stable hydrides in steel.¹ Due to its high mobility, hydrogen can easily diffuse through the lattice,² causing problems such as embrittlement. On the other hand, nitrogen dissolved in steel can increase yield and tensile strengths, decrease the ductility, and adversely affect the formability of ultralow-carbon cold rolled steel. Steel exposed to hydrogen at higher temperature and pressure can undergo hydrogen attack in the form of internal decarburization, resulting in marked reductions in ductility and strength.² When dissolved in excess of its solubility, hydrogen rejected by solid steel accrues in pinholes, thereby creating a high gas pressure. During hot working and subsequent cooling, the cumulative effect of hot working stresses and the high gas pressure in the pinholes near the surface can cause hairline cracks (flakes), leading to premature failure.

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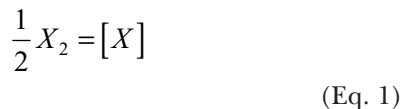


Hydrogen is picked up by the steel melt, typically from the absorbed moisture associated with the raw materials used in steelmaking. Other sources of hydrogen include hot metal (2–5 ppm) and scrap (2–7 ppm).³ At U. S. Steel, process data show increased levels of hydrogen, especially for the Q-BOP process, in which the natural gas (mainly CH₄) used as a tuyere coolant cracks to liberate gaseous hydrogen and subsequently dissolves into the liquid steel. In addition, ladle slag is commonly conditioned by adding lime-based fluxes to increase the efficiency of desulfurization, but such materials may be hydrated due to prolonged exposures to atmospheric moisture.⁴ Steelmaking additions such as carburizers and ferroalloys with high levels of nitrogen and hydrogen impurities can further increase the concentrations of hydrogen and nitrogen in liquid steel.⁴ Perhaps one of the largest sources of nitrogen is absorption from the atmosphere, which can occur through air bubbles entrained during tapping,⁵ through a spout eye exposed during argon stirring, or during any other form of interaction between liquid steel and atmospheric nitrogen. Besides hot metal and scrap, oxygen gas is another major raw material used in steelmaking which may have nitrogen as an impurity and add to the total nitrogen content of liquid steel. Natural gas is also known to contain significant nitrogen and can cause similar nitrogen pickup during the later stages of oxygen blow in a Q-BOP vessel.

The issues encountered in the measurement of hydrogen, and of nitrogen in making grades which require low nitrogen, are equally important. Furthermore, the evolution of surplus hydrogen and nitrogen during solidification not only can cause porosity in the steel, but the evolved gases can interact with the liquid mold flux layer in the continuous casting mold, which can induce a sticker-type breakout. In this study, the direct sources of hydrogen and nitrogen pickup in steel are identified, the thermodynamic calculations involved in accurate analyses of these gaseous species reviewed, and the impact of gas evolution at the continuous caster discussed.

Thermodynamic and Kinetic Considerations

Like other diatomic gases, hydrogen and nitrogen dissolve atomically in liquid iron according to the following reaction:



The dissolution of these gases in pure iron obeys Sievert's Law:

$$[\%X] = K_X \cdot (p_{x_2})^{\frac{1}{2}} \quad (\text{Eq. 2})$$

where

[%X] represents the weight percentage of dissolved hydrogen or nitrogen,

p_{x_2} is the partial pressure of hydrogen or nitrogen in the atmosphere and

K_X is the equilibrium constant for Equation 2.

The equilibrium constant K_X is obtained from the standard free energy of solution in pure liquid iron and is given by Equation 3 for hydrogen⁶ and Equation 4 for nitrogen,⁷ respectively:

$$\log K_H = -\frac{1,670}{T} - 1.68 \quad (\text{Eq. 3})$$

$$\log K_N = -\frac{188}{T} - 1.24 \quad (\text{Eq. 4})$$

where T is the absolute temperature in Kelvin (K). The presence of carbon in liquid iron is known to decrease the solubility of nitrogen and hydrogen. Figure 1 shows the hydrogen and nitrogen contents of iron-carbon alloys in equilibrium with 1.0 atmosphere of each of the respective gases.

The kinetics of nitrogen absorption and desorption in liquid iron have been studied by a number of researchers^{8–12} in the past and are believed to be well understood. Depending on the concentrations of surface-active elements such as oxygen and sulfur, the rate of nitrogen reaction with liquid iron is affected by different rate-controlling steps, as shown in Figure 2. At lower concentrations of these elements, the rate of nitrogen absorption in the liquid metal is controlled mainly by liquid phase mass transfer. At higher concentrations of oxygen and sulfur, the rate of nitrogen absorption is controlled primarily by chemical kinetics. The rate is second-order with respect to the nitrogen content in the melt, and the rate-controlling step is the dissociation of nitrogen molecules at the liquid metal surface. At intermediate levels of oxygen and sulfur, the rate shows mixed control, being limited by both chemical kinetics and mass transfer in the liquid phase. For high sulfur levels, the rate does not approach zero and a residual rate is observed.

The rate of transfer of nitrogen through the liquid phase boundary layer is expressed as:

$$J_N^{LPMT} = \frac{m_L \cdot \rho}{100 \cdot MW_{N_2}} \cdot (\%N_{surf} - \%N_{bulk}), \quad (\text{mol} / \text{cm}^2 \text{ s}) \quad (\text{Eq. 5})$$

where

m_L is the liquid phase mass transfer coefficient (cm/s),

ρ is the density of liquid metal (g/cm³),

$\%N_{surf}$ and $\%N_{bulk}$ are the nitrogen contents at the gas-liquid interface and in the bulk liquid, respectively, and

MW_{N_2} is the molecular weight of nitrogen (g/mol).

The rate of chemical reaction is represented by Equation 6:

$$J_N^C = k_a \cdot (p_{N_2}^{surf} - p_{N_2}^e), \left(\text{mol} / \text{cm}^2 \text{ s} \right) \quad (\text{Eq. 6})$$

where

k_a is the chemical rate constant ($\text{mol}/\text{cm}^2 \text{ s atm}$) and

$p_{N_2}^{surf}$ and $p_{N_2}^e$ are the nitrogen pressures at the gas-liquid metal interface and in equilibrium with the nitrogen in the metal, respectively.

$p_{N_2}^e$ can be calculated from the equilibrium of the nitrogen absorption reaction and is expressed as follows:

$$p_{N_2}^e = \frac{[\%N]^2 \cdot f_N^2}{K_N} \quad (\text{Eq. 7})$$

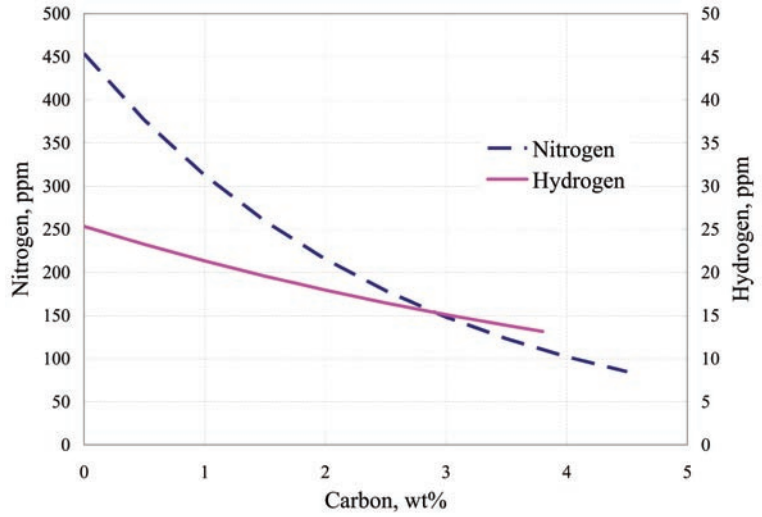
where f_N is the activity coefficient for nitrogen. The chemical rate constant, which incorporates the effect of the surface-active elements, is given by a simple site model, which implies ideal adsorption for oxygen and sulfur. The rate constant also includes a residual rate for higher sulfur concentrations and is expressed as:

$$k_a = \frac{k_b}{(1 + K_O h_O + K_S h_S)} + k_r \quad (\text{Eq. 8})$$

where

k_b is the rate constant for nitrogen on the bare iron surface ($\text{mol}/\text{cm}^2 \text{ s atm}$),

Figure 1



Solubilities of hydrogen and nitrogen (at 1.0 atm) in iron-carbon alloys at 1,550°C.

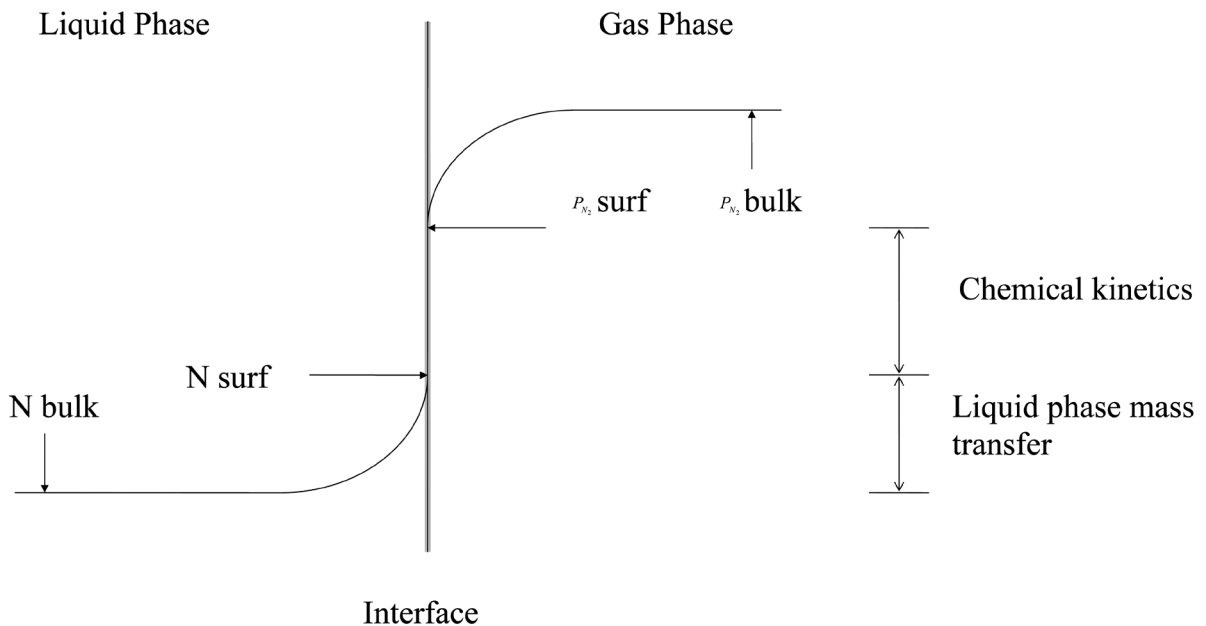
k_r is the residual rate constant,

K_O and K_S are the adsorption coefficients for oxygen and sulfur, respectively, and

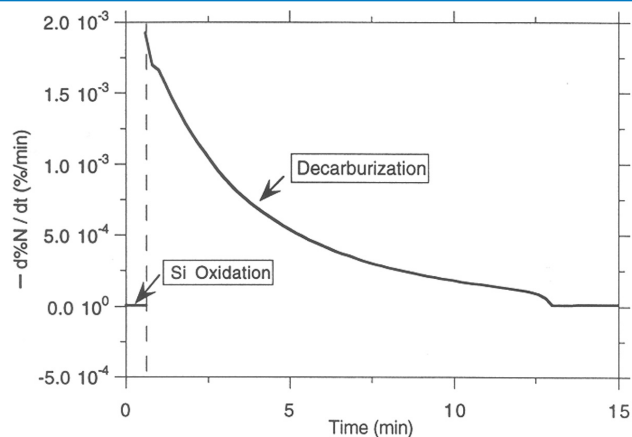
h_O and h_S are the activities of oxygen and sulfur in the 1 wt. % standard state.

In the case of hydrogen removal, the rate can be controlled by either diffusion of hydrogen in liquid iron (liquid phase mass transfer) or by saturation of gas bubbles with hydrogen. An equation similar to Equation 5 can be used to define the rate of liquid phase mass transfer for hydrogen. In the case of saturation of gas bubbles with hydrogen, gas bubbles rising through the bath are continually enriched with hydrogen, and the partial pressure inside the bubbles increases until it

Figure 2



Resistances to nitrogen absorption into liquid iron alloys.¹³

Figure 3Rate of nitrogen removal during the oxygen blow.¹⁴

reaches the hydrogen partial pressure in thermodynamic equilibrium with the dissolved hydrogen in the melt.

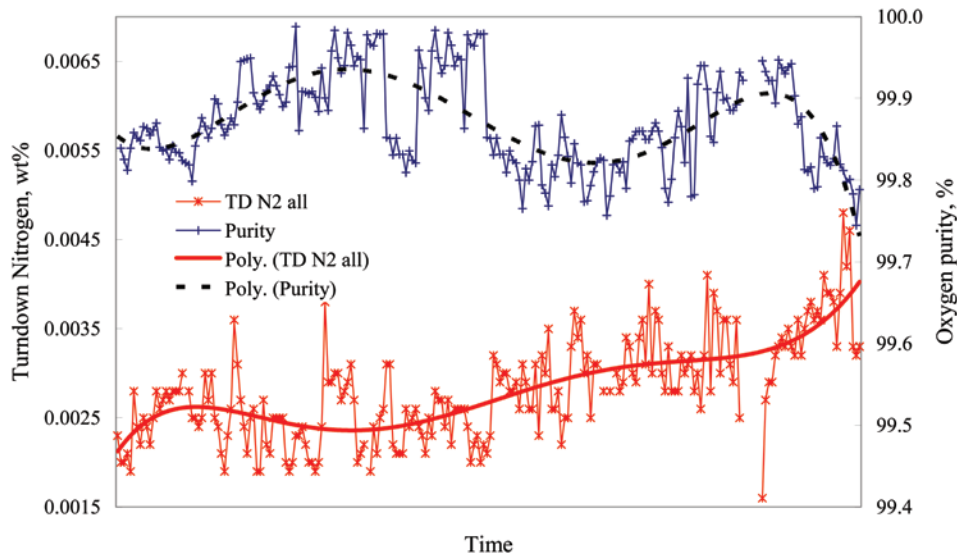
Reactions in the BOP and Q-BOP Vessels

The initial stages of the oxygen blow in a steelmaking vessel are dictated by silicon oxidation with minimal carbon removal. As the silicon level decreases, the oxygen starts reacting with carbon. The rate of decarburization increases until a constant rate, which is dictated by the oxygen blow rate, is achieved. Finally, at low carbon levels, the rate of carbon removal slows again and is controlled by diffusion of carbon from the metal bulk to the gas-metal interface. Desorption of dissolved hydrogen and nitrogen through the CO bubbles formed as a result of carbon oxidation is the primary mechanism for their removal. Figure 3 shows the rate of nitrogen removal during the oxygen blow, as predicted by a mixed control model developed by Goldstein and Fruehan.¹⁴ The results show that no nitrogen is removed during the initial phase of the blow when silicon oxidation is the

primary reaction. The rate of nitrogen removal jumps as soon as carbon oxidation commences. As the dissolved carbon content decreases, the decarburization rate, and therefore the CO evolution and nitrogen removal rates, also decrease. Similar behavior is expected with hydrogen removal during the course of the oxygen blow. Interestingly, it is worth mentioning that the solubility of both of these elements in liquid steel increases with decreasing carbon content. Hence, nitrogen and hydrogen pickup can take place during the last stages of the blow due to pickup from impurities in oxygen and natural gas, as discussed below.

Oxygen is a major raw material used in the steelmaking process. The presence of impurities in the oxygen stream will certainly affect the quality of liquid steel. Oxygen is commercially produced by fractional distillation of air under cryogenic conditions. In this process, air is separated into its major components: nitrogen, oxygen and argon. Among these gases, nitrogen has the lowest boiling point, followed by argon and then oxygen. As the temperature decreases, oxygen continues to liquefy, forming an oxygen-rich mixture in the bottom of the column, while most of the nitrogen and argon flow to the top as a vapor. For a sufficiently pure oxygen stream, the main impurity is argon, and the concentration of nitrogen impurity must be very low. Since it is uneconomical to transport huge volumes of oxygen in gaseous form, it is liquefied and transported in the liquid state. Nitrogen is usually used as a seal gas to prevent oxygen from contaminating the oil in the compressor. Leaks and unexpected operational issues can cause traces of nitrogen impurity in the oxygen stream. In cases in which the oxygen being used in the vessel has a significant amount of nitrogen impurity, the nitrogen content of liquid steel at the end of blow increases. Near the end of the blow, nitrogen present in the oxygen jet dissolves in the liquid bath when the nitrogen removal efficiency of the bath is reduced due to the lower CO generation rate.

Natural gas, which is used as a tuyere coolant in the Q-BOP, has significant nitrogen content (typically around 1%) and also generates hydrogen gas as a result of cracking. A similar mechanism can be postulated for nitrogen and hydrogen pickup from natural gas. High concentrations of surface-active elements such as oxygen in liquid steel, which exists toward the end of the blow, will likely inhibit nitrogen absorption and desorption at the same time. Figure 4 shows the oxygen purity and turndown nitrogen at a U. S. Steel Q-BOP shop. While most of the gas analyzers measure the purity and not the impurity level of oxygen, it is important to analyze oxygen for nitrogen

Figure 4

Oxygen purity and turndown nitrogen content at a U. S. Steel Q-BOP shop.

Table 1**Moisture and Hydrogen Contents of Different Steelmaking Additions at a U. S. Steel Q-BOP Shop**

Material	Moisture, wt. %	Combined water, wt. %	Hydrogen, wt. %
Quick lime (Q-BOP)	< 0.05	2.66	0.78
High-Cal lime (Q-BOP)	< 0.05	2.58	0.67
Pebble lime (LMF/degasser)	< 0.05	1.64	0.57
Cal-stone (Q-BOP)	< 0.05	1.46	0.54
Burnt lime, before dryer (Q-BOP)	< 0.05	2.09	0.54
Coke (Q-BOP)	0.38	1.26	0.73
Carbon wire (LMF/degasser)	< 0.05	1.44	0.41

concentration in particular. The oxygen purity levels in Figure 4 seem high. However, the gas analysis showed that the balance in this case was primarily nitrogen and not the expected argon, which is why higher nitrogen levels were noticed at turndown. In order to isolate such issues, it is recommended that oxygen sampling be performed at the air separation plant, as well as closer to the entry point in the steelmaking vessel. A gas chromatograph or a mass spectrometer can be used for real-time, on-site analyses of these gases.

Besides hot metal, the scrap that is added as a coolant and a source of iron in the BOP and Q-BOP vessels is also a source of nitrogen. The typical nitrogen content in scrap varies between 40 and 220 ppm.¹⁵ Heavy scrap melts later in the blow and contributes to the dissolved nitrogen. As the decarburization rate slows, it becomes increasingly difficult to remove the nitrogen entering the liquid bath toward the end of the oxygen blow.

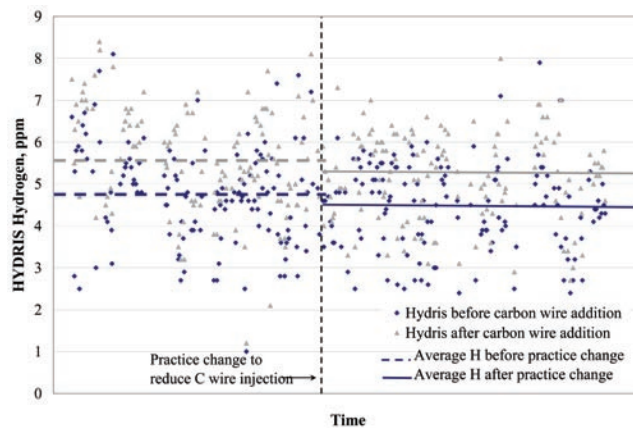
Pickup During Secondary Steelmaking

Raw materials and alloys added during the secondary steelmaking operation are also known to contribute to the dissolved nitrogen and hydrogen contents of steel. Among other sources, lime and coke are two important steelmaking additions that can contain hydrogen impurity. Moisture associated with these materials is also a direct source of hydrogen. Although steelmaking temperatures are significantly high to drive away most of the moisture and combined water, a fraction of this water in the form of hydrogen can still enter the molten metal and increase the dissolved hydrogen content of liquid steel. High hydrogen was being recorded in the tundish measurements at one of the U. S. Steel Q-BOP shops. It was hypothesized that one of the alloy or flux additions made at the ladle metallurgy facility (LMF) were contributing to the hydrogen in the steel. In order to isolate the source of hydrogen, different grades of lime and coke samples were collected for testing. These samples were analyzed for moisture; the combined water and hydrogen contents and the results are presented in Table 1.

Moisture is measured by heating the as-received sample to 105°C; combined water is measured subsequently by heating the sample further to 550°C; and hydrogen is measured on a dry sample. It is evident from Table 1 that the lime-based fluxes and carbon additions are significant sources of hydrogen. Based on

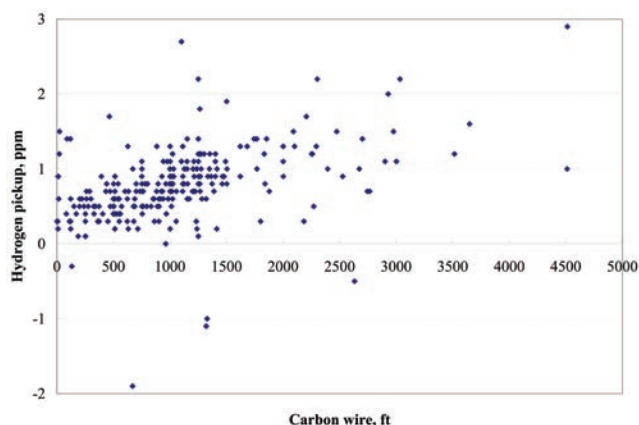
these observations, it was recommended that additions of coke and/or carbon wire should be minimized at the LMF, and that carbon chemistry control should be done by additions of these materials at tap. In response, a practice change was implemented to reduce the carbon wire injection at the LMF. Figure 5 shows the hydrogen content of liquid steel before and after the carbon wire injection. Also shown on the same graph are the average hydrogen values before and after the practice change. Figure 6 shows the hydrogen pickup as a function of carbon wire addition amount at the LMF. Despite scatter in the data, it is evident from both of these figures that reducing the wire injection amount lowered the hydrogen pickup.

Hydrogen pickup is aggravated under warm and humid weather conditions. It is known that the extent of hydrogen pickup strongly depends on the partial pressure of moisture in the air depends on the temperature and the relative humidity, the warm and humid summer days provide favorable conditions for hydrogen pickup from the atmosphere as compared to winter days. For the same reason, liquid steel exposed to the atmosphere is prone to hydrogen pickup. Similarly, nitrogen pickup can take place through atmospheric exposure in the form of air bubbles entrained during tapping and also

Figure 5

Hydrogen measurement before and after carbon wire addition at the LMF.

Figure 6



Hydrogen pickup as a function of carbon wire injection at the LMF.

through the spout eye during vigorous bottom stirring. CalSil additions and arcing in the LMF can also leave the liquid metal surface exposed to the atmosphere. The steel movement and exposure at the eye produce a favorable environment for atmospheric reaction and nitrogen absorption.

Although the purity of argon gas used as a stirring gas at the LMF is generally fairly high, the presence of nitrogen impurity, often as a result of air leaking into the gas stream, can lead to some pickup. One of the indicators of nitrogen pickup at the caster can be the fade in aluminum concentration. A high argon flowrate in the shroud can open an eye by removing the inert tundish covering powder. This, in addition to leaks in the shrouding system, can expose the liquid metal to the atmosphere and cause oxidation of dissolved aluminum and liquid iron. Such exposure also causes nitrogen absorption.

Measurement Issues

A number of U. S. Steel shops use the Hydrogen Direct Reading Immersion System (HYDRIS[®]) for on-line measurement of hydrogen in liquid steel at the steelmaking and casting facilities. HYDRIS is an immersion probe system that provides an in-situ determination of the hydrogen content of liquid steel. Theoretically, HYDRIS measures the partial pressure of hydrogen gas in equilibrium with the dissolved hydrogen in liquid steel. The HYDRIS unit converts the partial pressure reading into a hydrogen content (in ppm) using a K/f factor. The dissolution of hydrogen into liquid steel is given by Equation 1; the concentration of the hydrogen in the metal is given by Sievert's Law:

$$[H_{ppm}] = \frac{K}{f} (p_{H_2})^{\frac{1}{2}} \quad (\text{Eq. 9})$$

where K is the equilibrium constant and f is the activity coefficient of hydrogen. For the hydrogen partial pressure measured in mbar and the hydrogen content in ppm, the equilibrium constant K is expressed as:¹⁶

$$\log K = -\frac{1,900}{T} + 0.9201 \quad (\text{Eq. 10})$$

and the activity coefficient of hydrogen dissolved in liquid iron alloys is given as:

$$\log f = \sum e_H^j \cdot [\% j] \quad (\text{Eq. 11})$$

The value of the interaction coefficients, e_H^j , for the common alloying elements are shown in Table 2.

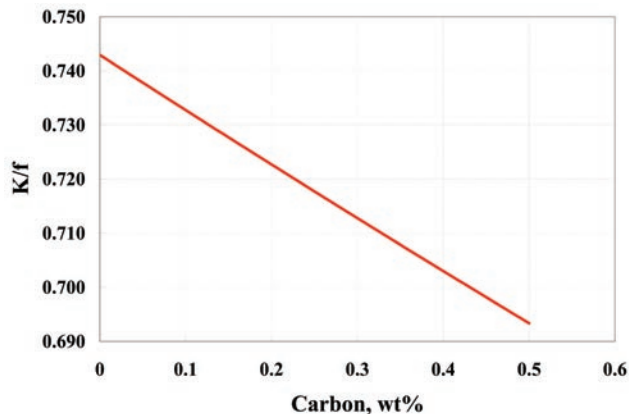
Table 2 shows that elements such as Cr, Mn, Ni and Cb have negative interaction coefficients. These elements will decrease the f value, while the other elements in the list will increase it. The HYDRIS unit calculates the hydrogen content using a constant K/f value of 0.75. Since K depends on temperature and f depends on the melt chemistry, for a more precise determination of the dissolved hydrogen, the K/f value needs to be corrected for the temperature and composition of the melt. Thermodynamic calculations show that for low carbon steel at typical steelmaking temperatures, the K/f factor is around 0.75 and decreases as the carbon content increases or the temperature decreases. Additionally, higher levels of silicon and aluminum will also decrease the K/f factor by increasing the activity coefficient. Figures 7–9 illustrate the effects of C, Si and Al on the K/f factor. Temperature is another important factor that affects the equilibrium constant, K , and therefore the K/f factor. Figure 10 shows the effect of different temperatures on the calculated values of K/f for a liquid steel chemistry with 0.04% each of C and Al and 0.3% each of Mn and Si.

The LECO[®] oxygen-nitrogen determinator has traditionally been the industry standard for nitrogen analysis. However, due to lower operating and maintenance costs, an optical emission spectrometer (OES) is often used for nitrogen analysis of steel samples (along with the full chemistry). A combination of LECO and Thermo Scientific ARL 4460 OES units is currently used

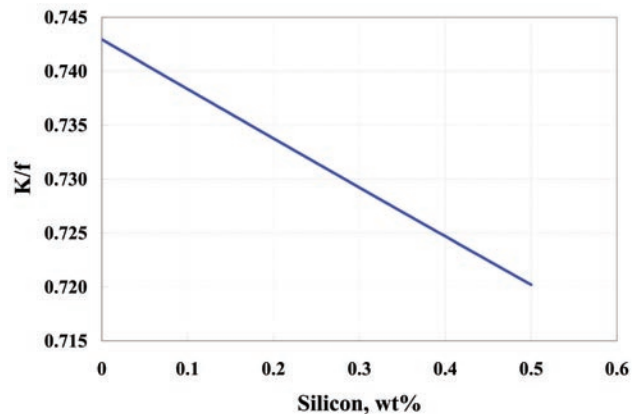
Table 2

Interaction Coefficients for Hydrogen Dissolved in Liquid Iron Alloys¹³

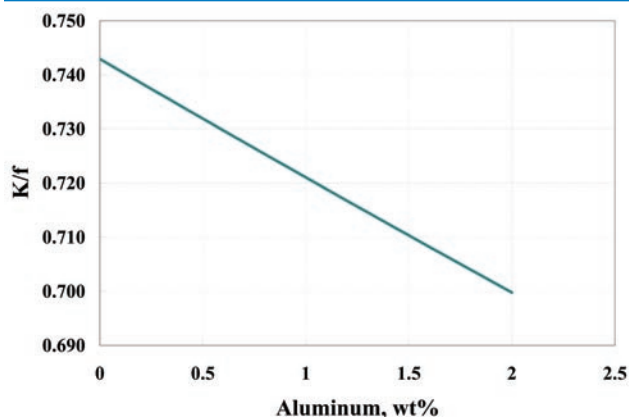
Alloying elements, j	Al	C	Cr	Mn	Ni	P	S	Si	Cu	Ti	B	Cb
e_H^j	0.013	0.060	-0.002	-0.001	-0.002	0.011	0.008	0.027	0.0005	0.08	0.05	-0.002

Figure 7

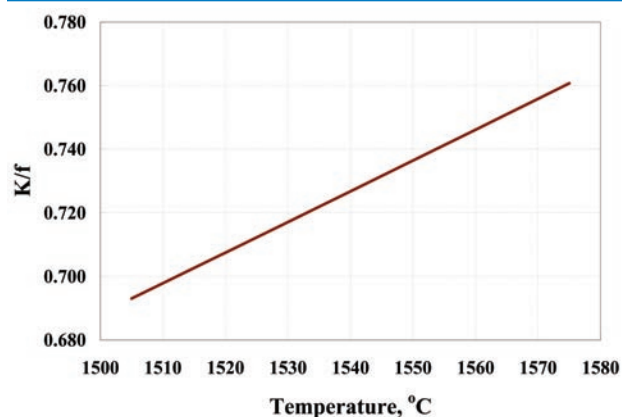
Influence of %C on the K/f factor.

Figure 8

Influence of %Si on the K/f factor.

Figure 9

Influence of %Al on the K/f factor.

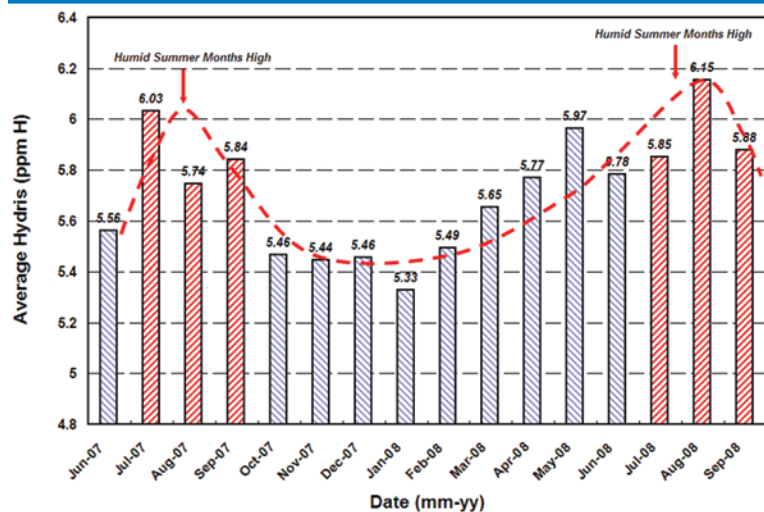
Figure 10

Influence of temperature on the K/f factor.

for nitrogen analysis at U. S. Steel plants. Despite the convenience, the accuracy of OES devices when used for nitrogen analysis is open to argument. The optical emission technique utilizes a high-energy spark created across an argon-filled gap between an electrode and the analysis sample. Among other things, the long-term stability of the OES is principally governed by the purity of the argon gas, the quality of the sample surface, the properties of the excitation unit, and the use of proper reference materials for control testing of the OES.

Argon Purity — Extensive use of argon by the optical emission spectrometer dictates that the argon supply must be very pure (grade 4, 99.99% purity, or higher). Ultrahigh-purity argon gas, with a maximum nitrogen impurity of 4 ppm, should be used in the OES unit. Argon should be free of contaminations such as nitrogen, oxygen, hydrocarbons and moisture by employing an efficient gas cleaning system. Most of the laboratories use stainless steel gas-carrying pipes instead of traditional copper tubing. An air inrush due to leaks (improper connections of seals and gaskets) or frequent changes of the gas-supplying source (gas tanks) can cause contamination with air. When using liquid argon tanks, a maximum fill of 80% of the tank volume should exist to ensure sufficient vapor phase.

Quality of the Sample Surface — Sample quality is another important variable with respect to nitrogen analysis. Poor-quality samples with pinholes and uneven surfaces allow atmospheric nitrogen to reside on the surface pockets and bias the analysis. Using proper samplers and ensuring a good sample quality are important for accurate and consistent analyses. The contact pressure exerted between the grinding surface and the specimen differs with different grinding techniques. Nonetheless, the grinding process may leave portions of the nitrogen-containing abrasive binding agent on the specimen surface, which can lead to inaccurate analyses. Samples from soft steel grades that are left with uneven surface roughness during grinding, if unfavorably positioned, allow micro-leaks to form between the specimen and the spark stand. Experience at U. S. Steel chemical laboratories has shown that the types of grid paper and grinding machine also affect the nitrogen analysis. A rotary grinder is preferred over a belt grinder, while a milling machine is expected to provide a decent surface finish. As a result of grinding, heat buildup in the sample requires the use of a coolant before the sample can be handled. Using water as a coolant, especially on an unfinished and porous sample surface, can contaminate the sample and provide an inaccurate analysis.

Figure 11

Monthly average hydrogen of all non-degassed heats over a 17-month period.

Excitation Unit — Extended use of the spectrometer may leave scratches and indentations in the sample holder stand. These are possible locations that allow air to enter the measuring gas in the course of the analysis, resulting in erroneous nitrogen readouts. To eliminate such inaccuracies, argon is used as a flushing gas to remove any air or other gas that may have entered the spark chamber. Sometimes the air residing in dead spaces, such as cracks and corners, persists despite the flushing action and can cause significant measurement errors. It is important, therefore, to regularly inspect the analysis chamber and keep it free of such shortcomings.

Reference Materials — According to ASTM Designation E305–89 on “Standard Practice for Establishing and Controlling Spectrochemical Analytical Curves,” the reference materials used for calibration of the OES should span the concentration ranges expected. Use of at least four reference materials is recommended for each curve. More than four reference materials should be used when the reference materials are close to each other in concentration. During the analysis process in an OES, each individual spark affects a different micro-surface. If the alloy is heterogeneous, scatter in the measurements is bound to happen. The presence of nitride precipitates can lead to unusually high nitrogen readouts in the spark excitation process and is responsible for the wide scatter in the measurements. Interference due to material homogeneity can often be overcome by repeating the analysis at higher spark energy levels. Visual inspection of the sample for obvious imperfections will ensure more consistent analyses.

Increased Hydrogen and the Impact on Continuous Casting

When elevated levels of hydrogen in steel are uncontrolled and sent to the continuous caster, significant lubrication issues can occur due to the evolution of hydrogen and its interaction with the mold flux. Typically, a Q-BOP shop producing a high-carbon grade without degassing and using the raw materials mentioned above can have hydrogen levels of above 8.5

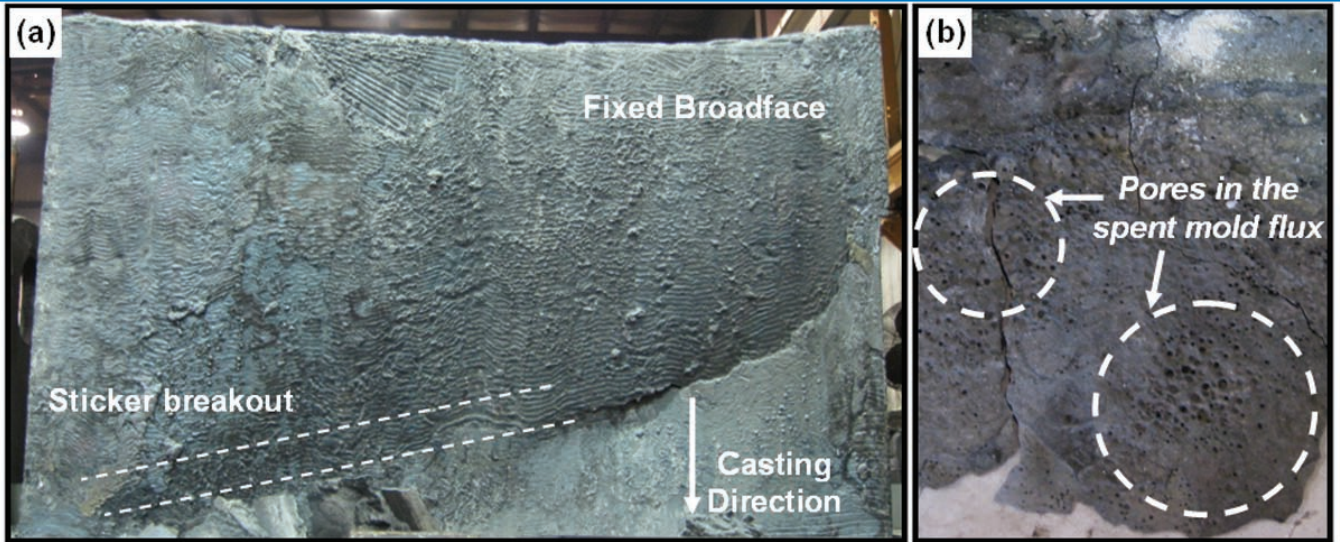
ppm. The first heat on a tundish at the caster can result in an additional pickup of more than 1 ppm. The combination of a heat at an elevated hydrogen level and the additional pickup in the tundish can result in conditions conducive for a caster breakout. Furthermore, although not directly realized in the steelmaking area, HYDRIS measurements taken at the caster over a 17-month period indicated that atmospheric conditions may also have an impact on the level of hydrogen at the caster. Figure 11 shows the monthly average hydrogen of all non-degassed grades taken after ladle open. Results show that the higher humidity conditions characteristic of the location resulted in higher average hydrogen levels. Furthermore, the past two hydrogen-related breakouts occurred in June and September, which suggests a need for increased awareness both in the steelmaking and casting operations during these seasonal conditions. Considering this particular pattern

of hydrogen levels, the shop has instituted preventive measures for moisture control in raw materials and modifications to the mold flux.

At high hydrogen levels, hydrogen in liquid steel can easily diffuse into the mold flux layer and significantly inhibit the lubrication abilities and result in a hydrogen-induced sticker-type breakout. Figure 12a shows a typical example of a hydrogen-induced sticker breakout that initiated on the narrow face of the slab, but wrapped around the broad face to lose containment after exiting the mold. Severe oscillation mark distortions are observed with the chevron mark pattern wrapping around the narrow face toward the fixed broad face. A sample of spent mold flux that was retrieved between the breakout shell and the copper mold is shown in Figure 12b, in which significant amounts of pinholes are observed on the surface that was facing the copper mold wall. This porosity of the mold flux layer inhibits heat transfer from the mold, which can be directly monitored by the drop in the value of BTU/lb. Although the BTU/lb. heat removal patterns during casting with high hydrogen content in steel are frequently used as an indication of issues in the mold, a drop in BTU/lb. was not observed for this particular event, indicating that changes in heat removal are not a necessary condition for hydrogen-induced sticker breakouts.

In addition to monitoring the BTU/lb. heat removal in the mold, breakout prevention systems using embedded thermocouples in the mold can be used to detect stickers associated with mold lubrication loss. The detailed mechanism of sticker detection using embedded thermocouples in the mold can be found in other publications.^{17–19} For this particular event, the temperature spike was not large enough to trigger an automatic slowdown. Empirical evidence has shown that hydrogen-related sticker-type breakouts can mask the temperature patterns of the sticker detection system so that the rise rate and rise amount of the temperatures do not reach the threshold values set for general sticker events. The temperature patterns that corresponded to the breakout shell are given in Figure 13.

Figure 12



Images of (a) the breakout shell after a hydrogen-related sticker breakout and (b) the spent mold flux taken from between the breakout shell and the copper mold. Note the significant amount of pores on the side facing the copper mold walls.

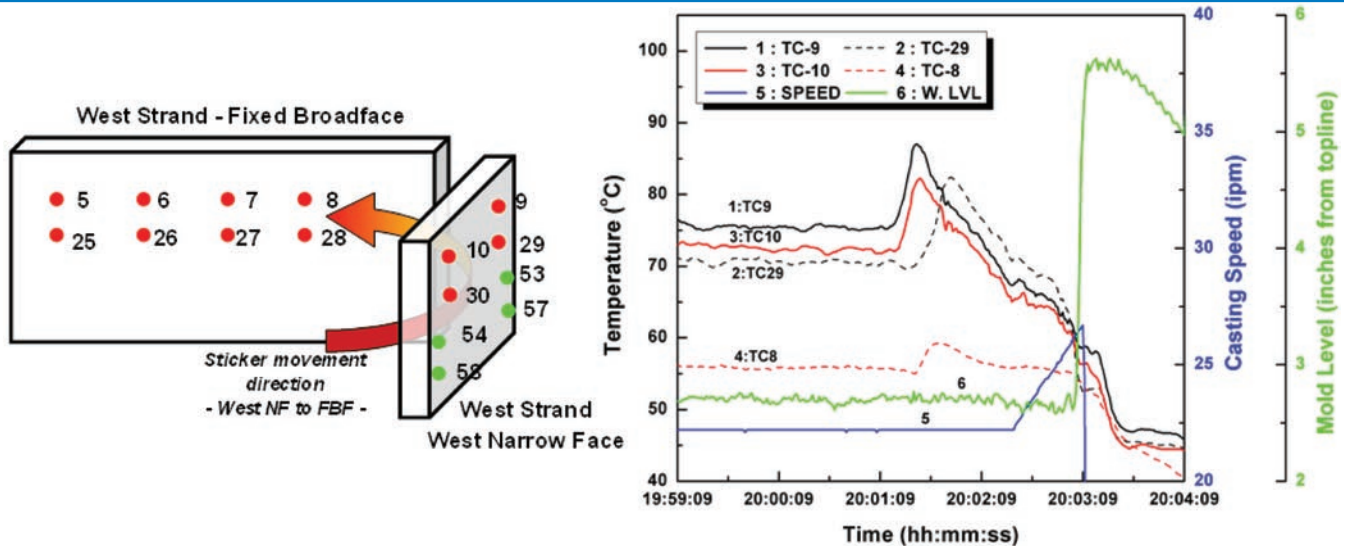
Although temperature spikes similar to a sticker are observed, the rise rate is not sufficient to trigger an automatic slowdown. TC-9 showed the initial spike in temperature, indicating that the initiation point of the sticker was likely near the narrow face.

Conclusions

The pickup of hydrogen and nitrogen in steel can take place through a number of sources, such as steelmaking additions, impure oxygen, and natural gas used as a Q-BOP tuyere coolant. Practice changes may be required to reduce the use of alloying materials with high levels of hydrogen and nitrogen. Quality specifications of alloys such as carbon wire, coke and lime must be established

to ensure low hydrogen impurity contents. When high concentrations of hydrogen are dissolved in liquid steel, the evolution of hydrogen gases while casting is likely and can potentially affect the performance of the mold flux. When the hydrogen reacts with the mold flux, gas pores can easily be formed and diminish heat transfer. With increased porosity in the mold flux layer, the temperature measurements from the breakout prevention system can also be masked to dampen the typical patterns observed for a sticker event. Precise quantitative analyses, particularly of hydrogen, and understanding of hydrogen-related effects on mold flux performance will allow the continuous casting operator to make preventive decisions in avoiding hydrogen-induced sticker breakouts.

Figure 13



Temperature measurements of embedded mold thermocouples from the breakout prevention system. The sticker initiated from the narrow face and moved toward the fixed broad face. Note the movements seen in TC-9 and TC-8.

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