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# Thermal Effect and Metallurgical Characteristics of Hydrogen Bottom Blowing in Top–Bottom Combined Blowing Converter

**Jianhua Liu [1], Hongbo Peng [1], Yang He [1,*], Xiaodong Yang [1], Hao Xu [1], Yaobin Hou [1] and Dali You [2]**

[1] Institute of Engineering Technology, University of Science and Technology Beijing, Beijing 065001, China
[2] Ferrous Metallurgy, Montanuniversitaet Leoben, 8700 Leoben, Austria
* Correspondence: heyang2020@ustb.edu.cn

**Abstract:** A new technology of hydrogen bottom blowing instead of traditional argon blowing in the current converter steelmaking process is proposed herein, in the aim of overcoming problems such as energy shortages caused by increased scrap charging, the low stirring intensity of bottom blowing, high $CO_2$ emissions, and endpoint carbon content control. The thermal effect and metallurgical characteristics of hydrogen bottom blowing were investigated based on the production data of a steelmaking converter in Pangang Group Xichang Steel & Vanadium Co., Ltd. This study shows that hydrogen bottom blowing at an intensity of 0.1–0.5 $m^3 \cdot min^{-1} \cdot t^{-1}$—rather than argon blowing at an intensity of 0.1 $m^3 \cdot min^{-1} \cdot t^{-1}$—can increase the smelting temperature by 16–73 K, increase the scrap charging ratio by 0.89–5.19%, and reduce $CO_2$ emissions by 19.79–115.96 kg per ton of steel. Intensive hydrogen blowing could significantly reduce the oxygen content of molten steel in the late stage of steelmaking and be beneficial to controlling oxygen at the endpoint. Hydrogen can also reduce the (FeO) content in slag, and the equilibrium partial pressure ratios of $H_2O/H_2$ for the reaction $H_2$ + (FeO) = $H_2O$ + Fe in the middle and late periods are 0.41 and 0.11, respectively. Hydrogen can also slightly suppress the decarbonization reaction in the late period of steelmaking, and the equilibrium partial pressure ratio of $H_2O/H_2$ for the reaction $H_2$ + (CO) = [C] + $H_2O$ in the late period is $9.65 \times 10^{-2}$, which means that hydrogen is beneficial in preventing the rapid decrease in [C] and, in turn, helps control the endpoint carbon content. By comparing the degree of the reaction $(P_2O_5) + 5H_2 = P_2(g) + 5H_2O$ and the reaction $(P_2O_5) + 5H_2 = 2[P] + 5H_2O$, it can be seen that intensive bottom-blown hydrogen may have a slight positive effect on slag gasification dephosphorization. The FactSage simulation results further verify the conclusions of the above analysis.

**Keywords:** converter; hydrogen; scrap ratio; carbon emissions; reduction of FeO; decarburization; deoxidization; bottom blowing

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## 1. Introduction

In recent years, there have been growing concerns of the urgency of addressing the enormous impact of $CO_2$ and other greenhouse gas emissions on the global ecological environment. As the industry with the second largest $CO_2$ emission, it is imperative that the steel industry reduces its carbon emissions [1,2]. To achieve the goal of green metallurgy, some new carbon reduction technologies such as microwave metallurgy [3–5], $CO_2$ metallurgy [6–9], and hydrogen metallurgy [10–18] were gradually studied and explored. $CO_2$ metallurgy has been applied in the fields of top–bottom combined blowing converters, electric arc furnaces [8], and AOD converter steelmaking [9]. Hydrogen metallurgy has been used in the area of ironmaking, such as hydrogen smelting reduction ironmaking [13] and hydrogen-rich blast furnace ironmaking [14], however, there have been few reports of the application of hydrogen metallurgy in the field of steelmaking.

Zhang Jie et al. proposed a technology for the efficient removal of inclusions with fine hydrogen bubbles in molten steel during the refining process by dissolving hydrogen in molten steel in advance and subsequent precipitation from the steel according to the characteristics of the rapid dissolution and rapid precipitation of hydrogen in molten steel under vacuum conditions [19]. Xing Wei also proposed blowing hydrogen through the RH up-nozzle to promote RH decarburization [20]. However, in these studies, hydrogen mainly played a role in promoting inclusion removal and decarburization. As the amount of hydrogen used in the above technologies was limited, only a miniscule reduction in $CO_2$ emission was realized in the steel production.

The expansion of scrap utilization in the steelmaking process is an important issue for $CO_2$ reduction in steel production [21]. However, to maintain the energy balance in the converter, extra energy is required for more scrap charging. Nakayama Steel started the operation of the NSR method (Nakayama Scrap Melting and Refining Process) in 2002 [22]. In this process, 100% scrap melting by coal top addition in a conventional top blowing converter was adopted. A KS converter was installed at Nippon Steel Hirohata Works for 100% scrap melting in the top- and bottom blowing converter, and coal was injected from the bottom blowing tuyeres. These technologies show the potential of $CO_2$ emission minimization in the converter steelmaking process, however, a large amount of coal was adopted to compensate for the energy shortage caused by excess scrap charging, which predictably produced a large amount of $CO_2$ emissions.

To solve the problems of energy shortage for excess scrap recycling in the converter, a new technology of intensive hydrogen bottom blowing was proposed in this study. In this technology, the oxidation heat of hydrogen is expected to provide supplement energy for scrap melting. At the same time, intensive hydrogen bottom blowing can also provide effective solutions for the problem of low stirring intensity in the current top–bottom combined blowing converter. Of course, the hydrogen reacts with [O] in the molten steel and oxides in slag and further affects the reactions in the converter, the process of steelmaking, and the quality of the steel.

In this paper, the material and heat balance of the traditional oxygen top blowing and argon bottom blowing converters were first calculated in the base of the compositions of the hot metal, scrap, and endpoint molten steel, which were used as a reference for comparison with the hydrogen bottom blowing converter. Then, the influence of the hydrogen bottom blowing on the energy balance and chemical reactions was studied with thermodynamic calculations, and the effects of the hydrogen blowing on the scrap charging ratio, $CO_2$ emissions, smelting temperature, and the compositions of melts in the smelting process were analyzed, which might help uncover the metallurgical characteristics of converter steelmaking with hydrogen bottom blowing. The thermodynamic analysis was further proven by FactSage calculation.

## 2. Thermal Effect of Hydrogen Bottom Blowing

### 2.1. Behaviors of Hydrogen in Converter

The possible metallurgical behaviors of a bottom-blown hydrogen in converter steelmaking are schematically shown in Figure 1. When $H_2$ is injected into molten steel from the converter bottom at high intensity instead of Ar, the mixture of the molten pool is significantly promoted, and the chemical reactions, mass, and heat transfer are accelerated. When the hydrogen bubbles reach the flame zone, $H_2$ reacts with $O_2$, and water vapor is generated. Meanwhile, a large amount of combustion heat is generated as well, which can be used for melting more scrap or increasing the temperature in the steelmaking process. On the other hand, hydrogen also reacts with molten steel in its floating process, especially with [O], which can be helpful in controlling the dissolved oxygen in molten steel and inhibiting the oxidation of easily oxidized elements such as manganese and chromium. There is a thick foam slag layer above the molten steel, and when hydrogen bubbles pass through it, the (FeO) in the slag is reduced to [Fe] by hydrogen bubbles, which is further transferred to the molten steel and reduce the iron loss in the steelmaking process. In the late period of smelting, there is a competitive oxidation process between hydrogen and [C] in the molten steel at a very high temperature, which is helpful in inhibiting the rapid drop of carbon content caused by the rapid decarbonization reaction and helpful for controlling endpoint carbon content.

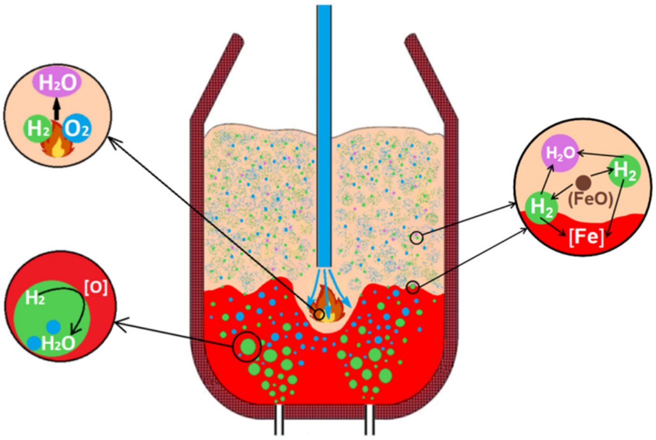

**Figure 1.** Metallurgical behaviors of hydrogen in converter.

### 2.2. *Effect of Hydrogen Blowing on Scrap Charging Ratio*

According to the energy balance in the steelmaking process, the scrap/hot metal charging ratio in the converter is determined by heat balance, i.e., the rest of the total formation heat is subtracted by the expenditure heat such as the physical heat for molten steel heating and the physical heat for slag formation and heating that can be used as the heat for scrap recycling, by which the scrap/hot metal charging ratio of the process can be calculated. On the basis of the heat balance of the traditional oxygen top blowing and argon bottom blowing converter (hereinafter referred to as the argon bottom blowing converter), the effect of hydrogen bottom blowing on the scrap/hot metal ratio in the steelmaking process was analyzed. In reference to the actual production data of an argon bottom blowing converter in Pangang Group Xichang Steel & Vanadium Co. Ltd, argon was blown into the converter from the bottom at a flow rate of 0.1 $m^3$ per minute for every ton of molten steel. The total blowing time was 17 min. The other basic process parameters of the production are listed in Tables 1 and 2.

**Table 1.** Compositions of hot metal and scrap (wt%).

| Elements<br>Materials | C | Si | Mn | P | S |
|---|---|---|---|---|---|
| Hot metal | 4.711 | 0.515 | 0.174 | 0.056 | 0.014 |
| Scrap | 0.18 | 0.25 | 0.55 | 0.03 | 0.03 |

**Table 2.** Temperatures of charging materials and products.

| Categories | Charging Materials | | | Products | | | |
|---|---|---|---|---|---|---|---|
| | Hot Metal | Scrap | Other Materials | Molten Steel | Slag | Dust | Converter Gas |
| $T/°C$ | 1310 | 25 | 25 | 1700 | 1700 | 1450 | 1450 |

According to the material balance and heat balance calculations, 128.8 kg cold scrap with a temperature of 298 K can be charged into the argon bottom blowing converter together with 1 t hot metal charging, and finally, 1031.6 kg molten steel can be produced. According to the calculations, the scrap/hot metal ratio for the converter charging is 11.41%, and the heat absorbed by 128.8 kg scrap for melting and the increasing temperature is 188,854.08 kJ, i.e., 124.3 kg scrap is recycled in every ton of molten steel produced and the heat for scrap recycling (named as an extra calorific value in this paper, $\Delta C_E$) which is 183,066.97 $kJ \cdot t^{-1}$ steel.

In steel production, the argon bottom blowing flow rate is 0.1 $m^3$ per minute for every ton of molten steel, and the total blowing time is 17 min. Therefore, the volume of argon blown into the converter for every ton of molten steel, $Q$, is calculated as $0.1 \times 17 = 1.7\ m^3$.

Argon does not react with other components in the converter and only plays a stirring role in the smelting process. However, when the heated argon is finally extracted from the top of the converter, a large amount of heat is taken away with it, which is not conducive to the temperature increase of the molten steel. This is why the amount of argon bottom blowing is usually maintained at a low level in the real converter steelmaking process. However, the hydrogen bottom blowing is different from that. Due to its combustion reaction with the oxygen injected from the top of the converter with the lance, hydrogen can provide additional heat. Intensive hydrogen blowing cannot only promote the temperature rising but also strengthen the stirring of the molten pool.

The heat consumed by the argon injected into the converter from the bottom $\Delta H_{\mathrm{Ar}}$, kJ, can be calculated by:

$$\Delta H_{\mathrm{Ar}} = \frac{Q}{0.0224} \times (T_S - T_0) \times C_H \tag{1}$$

where $T_S$ and $T_0$ are the smelting temperature and room temperature, in K, respectively, whilst $C_H$ is the thermal capacity of argon, $\mathrm{kJ \cdot K^{-1}}$.

For every ton of steel produced in the heat of Ar bottom blowing at an intensity of $0.1\ \mathrm{m^3 \cdot min^{-1} \cdot t^{-1}}$, $Q$ is 1.7 $m^3$. $T_S$ can be set as the median temperature of the molten pool in the whole steelmaking, 1723K, $T_0$ is 298K, and $C_H$ is 20.79 $\mathrm{kJ \cdot K^{-1} \cdot mol^{-1}}$ [23,24]. The heat consumed by argon is calculated as 2248.38 kJ.

Assuming that the bottom injecting nozzles are set near the center of the converter bottom, and the gaseous stream flowed up closely around the central axis of the converter and finally into the flame area, the injected hydrogen is fully burned with oxygen in the flame area of the converter. Then, replacing argon with the same amount of hydrogen, the extra generated calorific can be calculated by the sum of combustion heat of the hydrogen and heat extracted by argon:

$$\Delta H_{\mathrm{H_2-Ar}} = \frac{Q}{0.0224} \times \Delta H_{\mathrm{H_2O,m}} + \Delta H_{\mathrm{Ar}} \tag{2}$$

where $\Delta H_{\mathrm{H_2-Ar}}$ is the heat generated by the hydrogen bottom blowing instead of argon, kJ, and $\Delta H_{\mathrm{H_2O,m}}$ is the combustion heat of hydrogen per mol, kJ.

For every ton of steel produced in hydrogen bottom blowing instead of argon bottom blowing at an intensity of $0.1\ \mathrm{m^3 \cdot min^{-1} \cdot t^{-1}}$, the combustion heat of hydrogen and oxygen in the converter at 1723 K, $\Delta H_{\mathrm{H_2O,m}}$, is calculated as 183.50 kJ $\mathrm{mol^{-1}}$ with the thermodynamic data in reference [23]. The extra calorific generated caused by hydrogen bottom blowing is calculated as 16,174.72 kJ.

Furthermore, to strengthen the stirring effects of the bottom injection in the molten pool and provide more energy to the converter for more scrap recycling, the flow rate of hydrogen bottom blowing should be amplified. Hence, the extra calorific generated in the hydrogen bottom blowing converter compared with the traditional argon bottom blowing converter can be calculated as:

$$\Delta H_{\mathrm{H_2-Ar}} = \frac{Q}{0.0224} \times \Delta H_{\mathrm{H_2O,m}} \times \frac{f}{0.1} + \Delta H_{\mathrm{Ar}} \tag{3}$$

where $f$ is the intensity of hydrogen bottom blowing, $\mathrm{m^3 \cdot min^{-1} \cdot t^{-1}}$.

Replacing $Q$ in this equation with the actual value of 1.7 $m^3$ in the 210 t converter (CISDI GROUP CO., LTD, Chongqing, China) steelmaking in Pangang Group Xichang Steel & Vanadium Co. Ltd, the extra calorific generated in the hydrogen bottom blowing process can be calculated as:

$$\Delta H_{\mathrm{H_2-Ar}} = 13926.64 \times \frac{f}{0.1} + \Delta H_{\mathrm{Ar}} \tag{4}$$

According to the above analysis, it is clear that an extra calorific of 16,174.72 kJ per ton of molten steel is produced in the 210 t converter when the argon bottom blowing in 0.1 $m^3{\cdot}min^{-1}{\cdot}t^{-1}$ is replaced by hydrogen bottom blowing at the same intensity. Furthermore, when the hydrogen bottom blowing intensity is amplified, the extra calorific generated is also amplified, and the amplified rate is 13,926.64 kJ per 0.1 $m^3{\cdot}min^{-1}{\cdot}t^{-1}$ increment in hydrogen injection intensity.

With an increasing hydrogen injection rate in the converter bottom, a better stirring effect of the molten pool is realized. When the bottom blowing intensity reaches 10% of the top blowing intensity, the stirring effect can achieve that of the oxygen bottom-blown converter smelting, which is regarded as an ideal scene of the molten pool mixture for converter steelmaking. The top blowing oxygen flow rate of the 210 t converter in Pangang Group Xichang Steel & Vanadium Co., Ltd varies in the range of 38,000–46,000 $m^3{\cdot}h^{-1}$, which equals a blowing intensity of 3.02–3.65 $m^3{\cdot}min^{-1}{\cdot}t^{-1}$. Therefore, the upper limit of the hydrogen bottom blowing intensity for the converter can be set to 0.5 $m^3{\cdot}min^{-1}{\cdot}t^{-1}$, and the extra calorific value in the converter can be used for scrap recycling when argon bottom blowing is replaced with hydrogen blowing, $\Delta C_E$, is:

$$\Delta C_{\mathrm{E}} = 183066.97 + \Delta H_{\mathrm{H_2-Ar}} \tag{5}$$

According to the equation, the extra calorific value generated in the 210 t converter for the hydrogen bottom blowing with various intensities is calculated and shown in Figure 2.

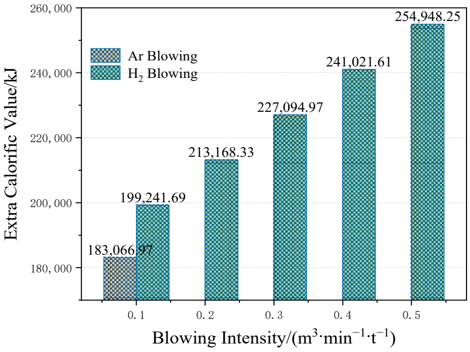

**Figure 2.** The extra calorific value generated in the 210 t converter for hydrogen bottom blowing at different intensities.

It can be seen that compared with argon blowing, hydrogen bottom blowing can provide more extra calorific, which can be used for scrap recycling and improve the scrap/hot metal ratio in the converter smelting. Assuming that all the extra calorific is used for scrap recycling, the amount of scrap and the change in scrap/hot metal ratio in the converter smelting are calculated according to the energy balance. The results are shown in Figures 3 and 4.

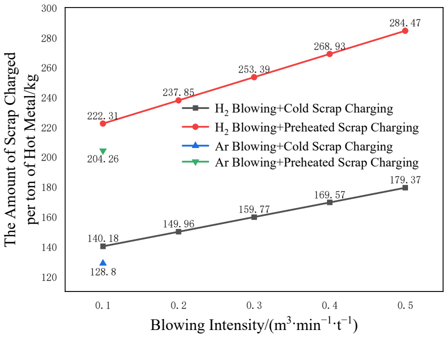

**Figure 3.** Influence of hydrogen injection intensity and scrap preheating on the charging amount of scrap.

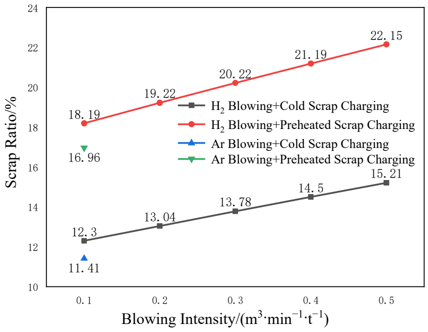

**Figure 4.** Influence of hydrogen injection intensity and scrap preheating on scrap/hot metal ratio in converter smelting.

In order to improve scrap recycling, in some Chinese steel plants, scrap is preheated before being charged into a converter. Therefore, the influence of hydrogen bottom blowing on the recycling of preheated scrap is also analyzed. The effect of bottom-blown hydrogen on the scrap addition amount and scrap ratio in converter smelting is studied when the preheating temperature is 1073 K. The calculation results are also shown in Figures 3 and 4.

According to the heat balance calculation, the charging ratios of cold and preheated scrap in the argon bottom blowing converter are 11.41% and 16.96%, respectively. Compared with argon blowing, the hydrogen bottom blowing in the converter can significantly increase the scrap charging ratio. With the intensity of 0.1 $m^3·min^{-1}·t^{-1}$, the hydrogen bottom blowing instead of argon bottom blowing can elevate the amount of cold scrap charging by 11.38 kg per ton of steel and elevate the charging ratio of cold scrap by 0.89%. While the hydrogen blowing intensity increases to 0.5 $m^3·min^{-1}·t^{-1}$, the amount of cold scrap charging can be increased by 50.57 kg per ton of steel, and the scrap ratio can be increased by 3.80%. On the other hand, the amount of preheated scrap charging can be increased by 18.05 kg per ton of steel, and the charging ratio of the preheated scrap can be increased by 1.23% with hydrogen bottom blowing instead of argon bottom blowing in 0.1 $m^3·min^{-1}·t^{-1}$. With the bottom blowing intensity increasing to 0.5 $m^3·min^{-1}·t^{-1}$, the amount of preheated scrap charging can be increased by 80.26 kg per ton of steel, and the ratio of preheated scrap charging can be increased by 5.19%.

### 2.3. Effect of Hydrogen Blowing on $CO_2$ Emission Reduction

$CO_2$ emissions are a severe problem in the traditional long process of iron- and steelmaking that use iron ore and hot metal as raw materials, however, these can be significantly reduced in a short process based on scrap recycling. In steel production, $CO_2$ emissions per ton of steel can be reduced by 22.36 kg when the scrap charging ratio, $R_S$, increases by 1% in converter steelmaking [25]. Therefore, compared with the traditional argon bottom blowing converter with an intensity of 0.1 $m^3·min^{-1}·t^{-1}$, the $CO_2$ emission reduction per ton of steel by substitution with intense hydrogen bottom blowing can be calculated.

$$M_{CO_2} = 22.36 \times \Delta R_S \tag{6}$$

where $M_{CO_2}$ is the mass of $CO_2$ emission reduction per ton of steel, $kg·t^{-1}$; and $\Delta R_S$ is the increase in the scrap charging ratio.

According to Equation (6), the possible $CO_2$ emission reduction with hydrogen bottom blowing application in the 210 t converter in Pangang Group Xichang Steel & Vanadium Co. Ltd can be calculated, as shown in Figure 5. The results show that hydrogen bottom blowing technology can significantly reduce the $CO_2$ emissions of the steelmaking process compared to argon bottom blowing. When the bottom blowing intensity is 0.1 $m^3·min^{-1}·t^{-1}$, the $CO_2$ emission can be reduced by 19.79 $kg·t^{-1}$ by hydrogen blowing instead of argon blowing. With the increase in hydrogen bottom blowing intensity, more $CO_2$ emissions are reduced. When the hydrogen bottom blowing intensity is 0.2, 0.3, 0.4 and 0.5 $m^3·min^{-1}·t^{-1}$, respectively, the $CO_2$ emission reduction is 36.45, 52.90, 69.05 and

84.95 kg·t$^{-1}$, respectively, compared with the steelmaking process of argon bottom blowing in the intensity of 0.1 m$^3$·min$^{-1}$·t$^{-1}$. Furthermore, if the scrap is preheated to 1073 K before being charged into the converter for steelmaking, more $CO_2$ emission reduction can be realized. It is shown in Figure 5 that the $CO_2$ emission reduction is 27.44, 50.40, 72.78, 94.63 and 115.96 kg·t$^{-1}$, corresponding to the steelmaking process with preheated scrap charging and with hydrogen bottom blowing intensities of 0.1, 0.2, 0.3, 0.4 and 0.5 m$^3$·min$^{-1}$·t$^{-1}$, respectively.

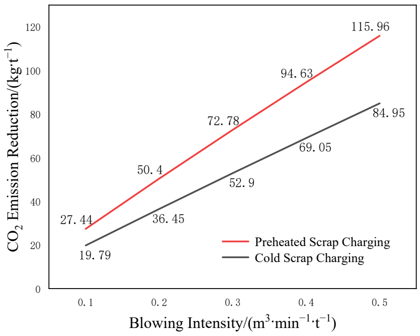

**Figure 5.** $CO_2$ emission reduction per ton of steel production by substituting argon bottom blowing with intense hydrogen bottom blowing.

### *2.4. Effect of Hydrogen Blowing on Smelting Temperature*

The extra calorific provided by the hydrogen combustion can be used not only for more scrap recycling but also to raise the temperature of molten steel and slag in the converter, especially when a high-endpoint temperature of molten steel is required for some grade steel production, such as in the production of some low-carbon steels with a BOF-RH-CC route.

In order to analyze the effect of the hydrogen bottom blowing process on the smelting temperature, it is assumed that the scrap/hot metal charging ratio remains unchanged, and all the extra calorific generated is only used for heating the molten steel and slag. Therefore, the temperature rise for hydrogen bottom blowing can be calculated as:

$$\Delta T = \frac{\Delta H_{\mathrm{H_2-Ar}}}{C_{\mathrm{Steel}} \times 1000 + C_{\mathrm{Slag}} \times M_{\mathrm{Slag}}} \tag{7}$$

where $\Delta T$ is the temperature rise, K; $C_{\mathrm{Steel}}$ is the heat capacity of molten steel, kJ·kg$^{-1}$·k$^{-1}$. $C_{\mathrm{Slag}}$ is the heat capacity of slag, kJ·kg$^{-1}$·k$^{-1}$; and $M_{\mathrm{Slag}}$ is the mass of slag for every ton of steelmaking, kg.

According to the material and energy balance calculation, in the 210 t converter in Pangang Group Xichang Steel & Vanadium Co. Ltd with traditional Ar bottom blowing at an intensity of 0.1 m$^3$·min$^{-1}$·t$^{-1}$, 118.0 kg slag and 110.83 kg slag are formed, respectively, for every ton of molten steel production with cold scrap and preheated scrap charging. According to the average heat capacity of molten steel of 0.837 kJ·kg$^{-1}$·k$^{-1}$ and the average heat capacity of the flux of 1.248 kJ·kg$^{-1}$·k$^{-1}$ provided by reference [23], the effect of the hydrogen bottom blowing process on the smelting temperature can simply be estimated with Equation (7).

For the scene of hydrogen bottom blowing replacing argon blowing at the same intensity of 0.1 m$^3$·min$^{-1}$·t$^{-1}$ in the 210 t converter, the increment in smelting temperature in the hydrogen bottom blowing converter charged with cold scrap at 298 K can be calculated as:

$$\Delta T_0 = 16174.72 \div (0.837 \times 1000 + 1.248 \times 118) = 16.43\mathrm{K} \tag{8}$$

Furthermore, the temperature increment for higher hydrogen blowing intensity can be calculated as:

$$\Delta T = \Delta T_0 + 13926.64f \div (0.837 \times 1000 + 1.248 \times 118) = 16.43 + 14.15f \tag{9}$$

On the other hand, when scrap is preheated to 1073 K and then charged into the converter, the argon bottom blowing is replaced with hydrogen blowing at the same intensity of 0.1 $m^3 \cdot min^{-1} \cdot t^{-1}$, and the temperature increment of the molten pool in the converter can be calculated as:

$$\Delta T_1 = 16174.72 \div (0.837 \times 1000 + 1.248 \times 110.83) = 16.58\text{K} \tag{10}$$

Additionally, the temperature increment for the preheated scrap charging and higher intensive hydrogen blowing can be calculated as:

$$\Delta T = \Delta T_1 + 13926.64 \times f \div (0.837 \times 110.6373 + 1.248 \times 12.2623) = 16.58 + 14.28f \tag{11}$$

Comparing the above equations, it is easy to find that the temperature increases for both cold scrap and preheated scrap charging are very close. Based on the above calculations, the temperature increments of molten pools in the steelmaking scenes of argon bottom blowing at an intensity of 0.1 $m^3 \cdot min^{-1} \cdot t^{-1}$ replaced by hydrogen bottom blowing in different intensities are shown in Figure 6.

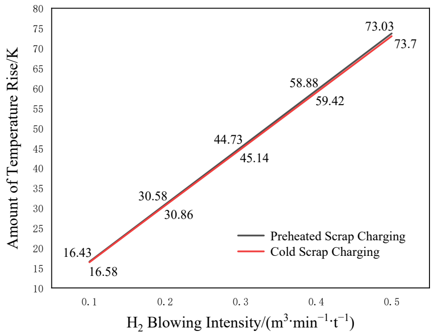

**Figure 6.** Effect of hydrogen bottom blowing at different intensities on the temperature of the molten pool.

Figure 6 shows that hydrogen bottom blowing can elevate the temperature of the melts remarkably, and the increment in smelting temperature can be 16–73 K, corresponding to the hydrogen bottom blowing at an intensity of 0.1–0.5 $m^3 \cdot min^{-1} \cdot t^{-1}$ instead of argon bottom blowing at an intensity of 0.1 $m^3 \cdot min^{-1} \cdot t^{-1}$.

It should be emphasized that all the above calculations are based on the premise that the injected hydrogen does not react with other components in the converter except $O_2$, and is completely burned by $O_2$ to heat the molten pool. In the actual production process, part of the hydrogen reacts with [O] in the molten steel and (FeO) and ($P_2O_5$) in slag as the bubble floating up through the molten pool in the converter, as indicated in Figure 1. Although these reactions are also exothermic reactions, and the reaction heat can also elevate the smelting temperature and promote scrap recycling, the values of the reaction heat are usually lower than those of the heat of the reaction of hydrogen with $O_2$. Therefore, the actual effects of the hydrogen bottom blowing process on the smelting temperature and scrap recycling are not so significant as in the above calculations.

It is difficult to determine how much of the injected hydrogen reacts with $O_2$, [O] in molten steel, and (FeO) in slag, as this depends on many factors, such as the compositions of the molten steel and slag, temperature, and sites of bottom injectors. Among all the factors, the sites of bottom injectors have a significant influence on the reaction of hydrogen with $O_2$. Usually, the bottom injectors are installed at approximately 0.5D in the bottom of a top–bottom blowing converter, where D is the diameter of the converter bottom.

The diameter of the impact pit formed in the molten pool by oxygen top blowing is also approximately 0.5D. Therefore, when hydrogen is injected into the converter, hydrogen bubbles float up in the molten pool and arrive at the edge of the oxygen impact pit, and part of the hydrogen reacts with the oxygen in the impact pit. If the bottom injectors are installed near the center of the bottom, then more hydrogen bubbles enter the impact pool and react with the oxygen. Otherwise, less hydrogen is burned by the oxygen in the impact pit. Thus, the behaviors of the bottom-blown hydrogen can be adjusted by the injector sites in the converter bottom, according to the comprehensive optimization based on the actual requirements of converter steelmaking on the stirring effect, heating, and control of [O], [P], and (FeO) in the molten pool, etc.

## 3. Thermodynamics of Hydrogen Reactions in Converter

As illustrated in Figure 1, the possible reactions of $H_2$ in the converter include reactions with [O] in the molten steel, reductions in some components in slag such as (FeO), (MnO), and ($P_2O_5$), in addition to the stirring of the molten pool and combustion with $O_2$. To analyze the reaction thermodynamics of hydrogen with components in the molten steel and flux, the standard Gibbs free energies of some relevant reactions in the hydrogen bottom blowing converter are summarized in Table 3. Among them, the standard Gibbs free energies of some reactions were obtained by calculations based on the standard Gibbs free energies of the reactions given in the references [6,9,12,13,17,26].

**Table 3.** Standard Gibbs free energies for some reactions related to hydrogen in the converter ($J \cdot mol^{-1}$).

| | |
|---|---|
| $H_2 + [O] = H_2O$ | $\Delta G^{\theta}{}_{1} = -130{,}350 + 58.77\ T$ |
| $H_2 + (FeO) = [Fe] + H_2O$ | $\Delta G^{\theta}{}_{2} = -18{,}010 + 12.04\ T$ |
| $2H_2 + (SiO_2) = [Si] + 2H_2O$ | $\Delta G^{\theta}{}_{3} = 841{,}378 - 104.12\ T$ |
| $H_2 + (MnO) = [Mn] + H_2O$ | $\Delta G^{\theta}{}_{4} = 420{,}734 - 70.63\ T$ |
| $[Si] + 2[O] = (SiO_2)$ | $\Delta G^{\theta}{}_{5} = -580{,}678 + 221.66\ T$ |
| $[Mn] + [O] = (MnO)$ | $\Delta G^{\theta}{}_{6} = -290{,}384 + 129.40\ T$ |
| $2[H] + [O] = H_2O$ | $\Delta G^{\theta}{}_{7} = -203{,}454 - 2.15\ T$ |
| $H_2 + CO = [C] + H_2O$ | $\Delta G^{\theta}{}_{8} = -107{,}987 + 98.40\ T$ |
| $(P_2O_5) + 5H_2 = P_2(g) + 5H_2O$ | $\Delta G^{\theta}{}_{9} = -68{,}966 + 62.91\ T$ |
| $(P_2O_5) + 5H_2 = 2[P] + 5H_2O$ | $\Delta G^{\theta}{}_{10} = 267{,}310 - 103.50\ T$ |
| $[C] + [O] = CO$ | $\Delta G^{\theta}{}_{11} = -22{,}363 - 39.63\ T$ |

To analyze the thermodynamics of the chemical reactions in the hydrogen bottom blowing converter, the compositions of molten steel in the early, middle, and late stages of a heat converter steelmaking process in the Xichang plant were selected for analysis and are shown in Table 4.

**Table 4.** Compositions of molten steel in the early, middle, and late periods in a heat melting (wt%).

| Elements<br>Time | [C] | [Si] | [Mn] | [P] | [S] | [Cr] | T/K |
|---|---|---|---|---|---|---|---|
| Early period | 4.711 | 0.515 | 0.174 | 0.056 | 0.014 | - | 1583 |
| Middle period | 2.735 | 0.01664 | 0.03814 | 0.04326 | 0.1719 | 0.01244 | 1690 |
| Late period | 0.060 | 0.014 | 0.060 | 0.020 | 0.020 | - | 1936 |

The activities of the components in the molten steel were calculated according to the Wagner model. The Wagner formula [23] for calculating the activity coefficients of solute elements in multivariate systems can be expressed as:

$$\lg f_i = \sum_{j=2}^{n} e_i^j [\%j] \qquad (12)$$

where $f_i$ is the activity coefficient of solute element $I$ and $e_i^j$ is the interaction coefficient of activity of solute element $i$.

The interaction coefficient of activity of elements in molten steel [23] is shown in Table 5.

**Table 5.** The interaction coefficient of activity, $e_i^j$, of elements in molten steel.

| j<br>i | **[C]** | **[Si]** | **[Mn]** | **[P]** | **[S]** | **[Cr]** |
|---|---|---|---|---|---|---|
| [C] | 0.140 | 0.080 | −0.012 | 0.051 | 0.046 | −0.024 |
| [Si] | 0.180 | 0.110 | 0.002 | 0.110 | 0.056 | −0.0003 |
| [Mn] | −0.070 | 0 | 0 | −0.0035 | −0.048 | - |
| [P] | 0.130 | 0.120 | 0 | 0.062 | 0.028 | −0.030 |
| [S] | 0.110 | 0.063 | −0.026 | 0.029 | −0.028 | −0.011 |
| [Cr] | −0.120 | −0.0043 | - | −0.035 | −0.020 | −0.0003 |

The calculation results of activities of elements in the molten steel in different melting periods are listed in Table 6.

**Table 6.** Activities of elements in molten steel in different melting periods.

| **Elements**<br>**Time** | **[C]** | **[Si]** | **[Mn]** | **[P]** | **[S]** | **[Cr]** | **T/K** |
|---|---|---|---|---|---|---|---|
| Early period | 23.72 | 4.205 | 0.081 | 0.267 | 0.049 | - | 1583 |
| Middle period | 6.769 | 0.0537 | 0.024 | 0.1 | 0.341 | 0.00577 | 1690 |
| Late period | 0.0615 | 0.0145 | 0.0593 | 0.0205 | 0.0203 | - | 1936 |

On the other hand, the compositions of the slags during the middle period and late heat periods are listed in Table 7. As the composition of slag in the early period of the converter process varies a lot and cannot stay stable, lime and other slag formers are continually charged into batches in this period, and a lot of [Si], [Mn], and [Fe] in the molten steel are rapidly oxidized into the slags, whilst the composition of the early period slag is not able to be set. The activities of the components during middle and late period slags are calculated by the FactSage software and listed in Table 8.

**Table 7.** Components of the slag during the middle and late periods in a heat converter process (wt%).

| **Components**<br>**Time** | **(CaO)** | **($SiO_2$)** | **(FeO)** | **(MgO)** | **(MnO)** | **($P_2O_5$)** | **T/K** |
|---|---|---|---|---|---|---|---|
| Middle period | 42 | 30 | 11 | 11 | 3 | 3 | 1690 |
| Late period | 56 | 23.6 | 9.6 | 7.4 | 1.7 | 1.7 | 1936 |

**Table 8.** Activities of components in slag.

| **Components**<br>**Time** | **(CaO)** | **($SiO_2$)** | **(FeO)** | **(MgO)** | **(MnO)** | **($P_2O_5$)** | **T/K** |
|---|---|---|---|---|---|---|---|
| Middle period | $6.000 \times 10^{-3}$ | $6.292 \times 10^{-3}$ | $4.794 \times 10^{-1}$ | $5.703 \times 10^{-2}$ | $5.311 \times 10^{-2}$ | $2.584 \times 10^{-18}$ | 1690 |
| Late period | $1.838 \times 10^{-1}$ | $9.538 \times 10^{-5}$ | $1.564 \times 10^{-1}$ | $1.526 \times 10^{-1}$ | $6.804 \times 10^{-2}$ | $1.475 \times 10^{-20}$ | 1936 |

### *3.1. Reaction of Hydrogen with [O] in Steel*

In converter smelting, oxygen is blown in from the top and constantly dissolved into the molten steel, and free oxygen in the molten steel keeps rising. When hydrogen is injected into the molten steel from the converter bottom, a number of hydrogen bubbles are generated and float up in the molten pool in the converter. Some of them react with the dissolved oxygen in the way of $H_2 + [O] = H_2O$, reducing the oxygen content in the molten steel. In order to analyze the possibility and degree of reaction, several scenes during the early, middle, and late periods of converter smelting with different [O] contents were set in Table 9, and the activities of [O] in the scenes were calculated by the Wagner model.

**Table 9.** Activities of [O] in molten steel in different scenes.

| (%O)/(wt%)<br>Time | 0.004 | 0.01 | 0.015 | 0.02 | 0.025 | 0.03 | 0.04 | 0.06 | 0.08 | 0.1 | 0.12 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Early period | $2.58 \times 10^{-5}$ | $6.44 \times 10^{-5}$ | - | - | - | - | - | - | - | - | - |
| Middle period | - | $5.55 \times 10^{-4}$ | $8.30 \times 10^{-4}$ | $1.10 \times 10^{-3}$ | $1.38 \times 10^{-3}$ | $1.65 \times 10^{-3}$ | - | - | - | - | - |
| Late period | - | - | - | $1.84 \times 10^{-2}$ | - | - | $3.70 \times 10^{-2}$ | $5.43 \times 10^{-2}$ | $7.17 \times 10^{-2}$ | $8.89 \times 10^{-2}$ | $1.06 \times 10^{-1}$ |

The Gibbs free energy of the reaction $H_2$ + [O] = $H_2O$ is:

$$\Delta G_1 = \Delta G_1^{\theta} + RT \ln \frac{P_{H_2O}}{P_{H_2} \cdot a_0} \tag{13}$$

where $\Delta G_1^{\theta}$ is the standard Gibbs free energy of the reaction, J; $T$ is the reaction temperature, K; $P_{H_2O}$ is the partial pressure of water vapor, kPa; $P_{H_2}$ is the partial pressure of hydrogen, kPa; and $a_0$ is the activity of [O] in molten steel. The thermodynamic constant $R$ is taken as 8.314 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$.

According to Equation (13), the possibility and extent of the reaction of hydrogen bubbles with [O] in the molten steel mainly depend on the activity of [O] and temperature. Based on the [O] content and temperature listed in Tables 7 and 9, the equilibrium ratios of the partial pressure of water and hydrogen, $\frac{P_{H_2O}}{P_{H_2}}$, in the hydrogen bubbles in different periods of the steelmaking process can be calculated (Figure 7).

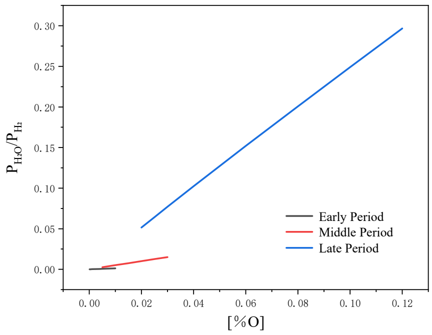

**Figure 7.** Equilibrium partial pressure ratio of water and hydrogen in the hydrogen bubbles in different steelmaking periods.

Figure 7 shows the extent of the $H_2$ + [O] = $H_2O$ reaction under the conditions of the corresponding [O] contents in the early, middle, and late stages of steelmaking. It is illustrated in Figure 7 that the [O] content in the early and middle stages of smelting is usually in the range of 100–300 × $10^{-6}$; the equilibrium ratio of the partial pressure of water and hydrogen is close to zero, which shows that the extent of the reaction of hydrogen bubbles with [O] in the molten steel is low. The hydrogen bottom blowing has little effect on the [O] of molten steel in the early and middle steelmaking stages.

However, in the late steelmaking stage, the [O] content is much higher and usually in the range of 400–1200 × $10^{-6}$. It is easier for the hydrogen bubbles to react with the [O] in molten steel during the floatation of the hydrogen bubbles in steel, which is helpful in controlling the increase in the dissolved oxygen in the late steelmaking stage. Figure 7 shows that the equilibrium partial pressure ratio of water and hydrogen in hydrogen bubbles is 0.10219 when the [O] content reaches 400 × $10^{-6}$ in the late stage of the steelmaking process, which means that approximately 9.27% of $H_2$ in the bubbles are oxidized into water vapor when the reaction reaches equilibrium, while when the [O] content in the molten steel comes to 1200 × $10^{-6}$, the equilibrium partial pressure ratio of water and hydrogen in the hydrogen bubbles is 0.2968, and approximately 22.89% of the $H_2$ in the bubble is oxidized into water vapor. Therefore, in the late stage of hydrogen bottom blowing converter steelmaking, a large amount of bottom-blown hydrogen reacts with the dissolved oxygen in the molten steel, which inhibits the rapid increase in oxygen content in the molten steel and is conducive to controlling the reaction rate of carbon and oxygen and preventing the rapid dropping of carbon content at the end of smelting, and is significantly more beneficial for the endpoint controlling of converter steelmaking.

On the other hand, the decrease in [O] in molten steel at the end of converter steelmaking significantly reduces the amount of deoxidizer in the subsequent refining process. This further reduces the numbers of inclusions generated in the steel and improve the cleanliness of the steel, which may reduce the $CO_2$ emission to a certain extent in the converter steelmaking process.

### *3.2. Reaction of Hydrogen with Components in Slag*

In the converter steelmaking process, the bubblization of slag is serious. There is a thick layer of slag above the molten steel, especially during the middle and late periods of the process. Therefore, the hydrogen bubbles must pass through the thick foaming slag. With the higher viscosity and lower density of the slag compared with steel, the hydrogen bubbles take more time to pass through the slag layer and react with some oxides in slag, as illustrated in Figure 1.

#### 3.2.1. Reaction of Hydrogen with (FeO) in Slag

(FeO) is one of the essential components in slag which has high oxibility, and its content in it usually represents the oxidizing capacity of the slag. When hydrogen bubbles pass through the foaming slag, the reaction $H_2$ + (FeO) = [Fe] + $H_2O$ takes place.

The Gibbs free energy of the reaction $H_2$ + (FeO) = [Fe] + $H_2O$ is:

$$\Delta G_2 = \Delta G_2^{\theta} + RT\ln\frac{P_{H_2O}\cdot a_{Fe}}{P_{H_2}\cdot a_{FeO}} \tag{14}$$

where $\Delta G_2^{\theta}$ is the standard Gibbs free energy of the reaction, J; $a_{Fe}$ is the activity of [Fe] and can be set as 1; and $a_{FeO}$ is the activity of (FeO).

According to the activities of (FeO) in the middle and late periods of steelmaking listed in Table 8, the equilibrium partial pressure ratio of water and hydrogen for a $H_2$ + (FeO) = [Fe] + $H_2O$ reaction can be calculated. Table 10 shows that the values of equilibrium $\frac{P_{H_2O}}{P_{H_2}}$ during the middle and late periods of the process are 0.41 and 0.11, respectively, which means that hydrogen can reduce (FeO) in slag to a certain extent in the middle and later stages of converter smelting, control the oxibility of slag, and reduce the iron loss.

**Table 10.** Equilibrium partial pressure ratio of water and hydrogen for reaction $H_2$ + (FeO) = [Fe] + $H_2O$.

| Time<br>Reaction | Middle Period | Late Period |
|---|---|---|
| $H_2$ + (FeO) = [Fe] = $H_2O$ | 0.41 | 0.11 |

In the real steelmaking process, before arriving at the slag and reacting with (FeO), the bottom-blown hydrogen must first pass through the molten steel. In this process, some hydrogen bubbles have already reacted with [O] in molten steel, which will have a suppression effect on $H_2$ + (FeO) = [Fe] + $H_2O$. It is, however, difficult to determine how much of the hydrogen will react with (FeO) in the slag or [O] in the molten steel. This reaction process is influenced by the bottom injecting rate, the structure of the injectors, the heights of the molten steel and slag, the compositions and characters of the steel and slag, etc. However, the two reactions contribute to the reduction in the (FeO) content in slag, as (FeO) and [O] have a close relationship with the following reaction:

$$(\mathrm{FeO}) = [\mathrm{Fe}] + [\mathrm{O}] \tag{15}$$

Additionally, the contents of [O] and (FeO) have a thermodynamic equilibrium relationship [20]:

$$\lg K^{\theta} = \lg \frac{[\%\mathrm{O}]}{x_{\mathrm{FeO}} \cdot \gamma_{\mathrm{FeO}}} = -\frac{6320}{T} + 2.734 \tag{16}$$

where $[\%\mathrm{O}]$ is the content of [O] in molten steel, wt%; $x_{\mathrm{FeO}}$ is the mole fraction of FeO in molten steel, mol·$\mathrm{L}^{-1}$; and $\gamma_{\mathrm{FeO}}$ is the Raoult activity coefficient of FeO. The activity of (FeO), i.e., the product of $x_{\mathrm{FeO}}$ and $\gamma_{\mathrm{FeO}}$, is given in Table 8.

Equation (16) indicates that the content of (FeO) has an equilibrium relationship with the content of [O] in molten steel, and a variation in [O] content results in the corresponding variation in (FeO) in slag. Therefore, the hydrogen bottom blowing can also reduce the (FeO) in slag by indirectly reacting with [O] in molten steel.

### 3.2.2. Reaction of Hydrogen with ($SiO_2$)

Whether hydrogen can reduce ($SiO_2$) in slag and further affect its ($SiO_2$) and [Si] contents is an interesting question. The thermodynamic reaction $2H_2$ + ($SiO_2$) = $2H_2O$ + [Si] is analyzed based on the activities in Tables 6 and 8 and the standard Gibbs free energy in Table 3, and the equilibrium partial pressure ratios of water and hydrogen in the middle and late periods are calculated and listed in Table 11.

**Table 11.** Equilibrium partial pressure ratios of water and hydrogen for $2H_2$ + ($SiO_2$) = $2H_2O$ + [Si].

| Time / Reaction | Middle Period | Late Period |
|---|---|---|
| $2H_2 + (SiO_2) = 2H_2O + [Si]$ | $7.07 \times 10^{-12}$ | $1.60 \times 10^{-10}$ |

Table 11 shows that the equilibrium partial pressure ratios of water and hydrogen for the reaction between hydrogen and ($SiO_2$) during the middle and late periods are both minimal, which means that the reaction of $2H_2$ + ($SiO_2$) = $2H_2O$ + [Si] does not take place during the middle and late periods of steelmaking. Hydrogen bottom blowing is not able to reduce silica in slag.

### 3.2.3. Reaction of Hydrogen with (MnO)

Manganese is an important alloying element, so the thermodynamics of the reaction of hydrogen with (MnO) in slag, $H_2$ + (MnO) = [Mn] + $H_2O$, is an interesting topic to be studied. The equilibrium partial pressure ratios of water and hydrogen during the middle and late periods of the steelmaking process are calculated based on the standard Gibbs free energy in Table 3, as well as the temperature and activity of [Mn] and (MnO) in Tables 6 and 8, respectively. The results are listed in Table 12.

**Table 12.** Equilibrium ratios of water and hydrogen for reaction $H_2$ + (MnO) = [Mn] + $H_2O$.

| Time / Reaction | Middle Period | Late Period |
|---|---|---|
| $H_2 + (MnO) = [Mn] + H_2O$ | $1.15 \times 10^{-9}$ | $5.60 \times 10^{-8}$ |

It is disappointing to find that the partial pressure ratios of water and hydrogen during the middle and late periods of the steelmaking process are very small. It can be considered that the degree of the reaction $H_2$ + (MnO) = [Mn] + $H_2O$ is very low, and that hydrogen blowing has no obvious reduction effect on manganese oxide in slag.

On the other hand, it can be seen from Tables 5 and 7 that the manganese content in the molten steel in the late period of the converter steelmaking increases, while the content of manganese oxide decreases compared with that in the middle stage. This is because, in the late stage of converter smelting, with the increase in slag basicity and temperature, the reduced ability of carbon in the molten steel increases. Therefore, a [C] + (MnO) = [Mn] + CO reaction takes place at the interface between steel and slag in the converter, and (MnO) in slag is partially reduced by carbon in the molten steel, resulting in an apparent manganese return in molten steel. Hydrogen bottom blowing can accelerate the reaction to some extent. When hydrogen bubbles arrive at the steel–slag interface, the partial pressure of CO in the bubbles is very low. The bubbles are equivalent to some finely dispersed vacuum chambers, which cannot only improve the thermodynamic conditions for the reaction between carbon and (MnO) but also the kinetic conditions by providing a CO bubble nucleus. Thus, hydrogen bottom blowing may promote the reduction kinetics of (MnO) in slag.

### 3.2.4. Reaction of Hydrogen with ($P_2O_5$)

Phosphorus is usually a detrimental element in most steel grades, and dephosphorization is an important task in converter steelmaking. In the steelmaking process, the phosphorus gradually accumulates in slag by the reaction between slag and molten steel, and the phosphorus is progressively removed from steel.

When $H_2$ bubbles pass through the foaming slag, some phosphorus oxides in slag may be reduced by hydrogen to elementary phosphorus. As the vaporization temperature of phosphorus allotropes is much lower than the smelting temperature and the phosphorus vapor $P_4$ is converted to $P_2$ when it is above 1560 K [27], some phosphorus is in the state of gaseous $P_2$ in the hydrogen bubbles—and further sucked away together with the converter off the gas. As such, the reaction equation of hydrogen with ($P_2O_5$) in slag can be expressed as:

$$(P_2O_5) + 5H_2 = P_2(g) + 5H_2O \tag{17}$$

On the other hand, the solubility of phosphorus in molten steel is high, and the phosphorus may dissolve in the molten steel drops. Thus, the reduction in ($P_2O_5$) in slag by hydrogen may also proceed in the following way:

$$(P_2O_5) + 5H_2 = 2[P] + 5H_2O \tag{18}$$

The standard Gibbs free energies for the reactions (17) and (18) are calculated and listed in Table 3. Referring to Guo Ruihua's research on the dephosphorization of converter slag gasification [26], the partial pressure of phosphorus in converter gas, $P_{P_2}$, is 0.005~0.01 kPa. Combined with the value of $a_{P_2O_5}$ shown in Table 8, the thermodynamics of the reaction between hydrogen and ($P_2O_5$) in slag can be analyzed, and the equilibrium ratios of water and hydrogen for reaction during the middle and late periods of the converter steelmaking are calculated and shown in Table 13.

**Table 13.** Equilibrium ratios of water and hydrogen for the reactions ($P_2O_5$) + 5$H_2$ = $P_2$(g) + 5$H_2O$ and ($P_2O_5$) + 5$H_2$ = 2[P] + 5$H_2O$.

| Reaction \ Time | Middle Period | Late Period |
|---|---|---|
| ($P_2O_5$) + 5$H_2$ = $P_2$(g) + 5$H_2O$ | $4.48 \times 10^{-4}$~$5.15 \times 10^{-4}$ | $1.41 \times 10^{-4}$~$1.62 \times 10^{-4}$ |
| ($P_2O_5$) + 5$H_2$ = 2[P] + 5$H_2O$ | $2.05 \times 10^{-4}$ | $2.23 \times 10^{-4}$ |

Table 13 shows that the equilibrium ratios of water and hydrogen for the reactions ($P_2O_5$) + 5$H_2$ = $P_2$(g) + 5$H_2O$ and ($P_2O_5$) + 5$H_2$ = 2[P] + 5$H_2O$ during the middle and late periods are low and in the same order of magnitude. This means that the reactions of $H_2$ with ($P_2O_5$) to generate gaseous $P_2$ and [P] are both difficult.

On the other hand, the reaction ($P_2O_5$) + 5$H_2$ = 2[P] + 5$H_2O$ is a three-phase reaction of steel–slag–gas, which requires that the hydrogen bubbles react with ($P_2O_5$) at the gas–slag–steel interface, so that the generated [P] can enter the molten steel. Obviously, the reaction conditions are harsh as the interface of the gas–slag–steel interface is limited in the foaming slag. Evidently, the slag–steel interface in the melt pool can provide a good chance for the coexistence of gas–slag–steel when the hydrogen bubbles pass through the interface. However, compared with the time for hydrogen floating in the foaming slag, the time of hydrogen bubbles across the slag–steel interface is very short, so the window time for the reaction $(P_2O_5) + 5H_2 = 2[P] + 5H_2O$ is also very short. This indicates that the rephosphorization caused by $(P_2O_5) + 5H_2 = 2[P] + 5H_2O$ is very limited. On the other hand, the reaction $(P_2O_5) + 5H_2 = P_2(g) + 5H_2O$ is a gas–slag diphase reaction. Due to the high viscosity of the foaming slag, the hydrogen bubbles stay in the slag for a long time, which can greatly promote the gaseous dephosphorization reaction. Therefore, hydrogen blowing is more likely to promote the gaseous dephosphorization of slag rather than rephosphorization.

## *3.3. Effect of Hydrogen on Oxidation Reactions in Molten Steel*

### 3.3.1. Effect of Hydrogen on Decarburization Process

The decarburization reaction $[C] + [O] = CO$ is the most critical reaction in the converter and takes place in the whole process of converter steelmaking. In a hydrogen bottom blowing converter, hydrogen bubbles also react with [O] during their floating up in the molten steel and further affect the decarburization reaction. The influence of the reaction $H_2 + [O] = H_2O$ on the decarburization reaction $[C] + [O] = CO$ can be analyzed with the thermodynamic of conjugate reaction $H_2 + CO = [C] + H_2O$. The Gibbs free energy of the reaction is:

$$\Delta G_8 = \Delta G_8^{\theta} + RT \ln \frac{P_{H_2O} \cdot a_C}{P_{H_2} \cdot P_{CO}} \tag{19}$$

where $\Delta G_8^{\theta}$ is the standard Gibbs free energy of the reaction, J; $a_C$ is the activity of [C]; and $P_{CO}$ is the gas-phase partial pressure of carbon monoxide, kPa.

$P_{CO}$ in the converter is usually approximately 1 atm. The temperatures and values of $a_C$ during the early, middle, and late periods of converter steelmaking are listed in Table 6. Thus, the equilibrium partial pressure ratios of water and hydrogen in the floating bubbles in the steelmaking process, $\frac{P_{H_2O}}{P_{H_2}}$, can be analyzed, and the results are shown in Table 14.

**Table 14.** Equilibrium partial pressure ratios of water and hydrogen for reaction $H_2 + CO = [C] + H_2O$.

| Reaction \ Time | Early Period | Middle Period | Late Period |
|---|---|---|---|
| $H_2 + CO = [C] + H_2O$ | $1.12 \times 10^{-3}$ | $2.33 \times 10^{-3}$ | $9.65 \times 10^{-2}$ |

Table 14 shows that, as the converter blowing process proceeds, the [C] content in the steel gradually decreases, and the equilibrium of the $H_2 + CO = [C] + H_2O$ reaction moves towards the right side and the value of equilibrium $\frac{P_{H_2O}}{P_{H_2}}$ increases. During the early and middle periods of steelmaking, the equilibrium partial pressure ratios of water and hydrogen are $1.12 \times 10^{-3}$ and $2.33 \times 10^{-3}$, respectively, which means that less water is generated in the bubbles. The effects of hydrogen on the decarbonization reaction are extremely minute.

In the late period, however, the equilibrium partial pressure ratio increases to $9.65 \times 10^{-2}$, which means that when the conjugate reaction reaches equilibrium, 8.80% of hydrogen in the bubbles reacts with water. The decarbonization reaction is slightly suppressed. In fact, in the current converter steelmaking process, due to the extremely high temperature of the melting pool in the late period of smelting, decarbonization takes place rapidly, so it is difficult to accurately control the carbon content at the endpoint. Bottom blowing hydrogen helps reduce the oxibility of the molten pool in the later period of converter smelting and is beneficial in delaying the excessively rapid oxidation of carbon. This is very beneficial to the control of the carbon content at the endpoint of converter smelting. Overall, hydrogen bottom blowing has a slight beneficial effect in terms of controlling end decarbonization.

### 3.3.2. Manganese-Preserving Effect of Hydrogen

In early converter smelting, the temperature of the melt pool in the converter is low. Silicon and manganese in molten steel are preferentially oxidized, and the drop in their contents is rapid. However, with hydrogen bottom blowing, hydrogen can suppress the rapid increase in the dissolved oxygen content in steel, which may bridle the reaction [Mn] + [O] = (MnO) to a certain extent. At the same time, due to the oxidation of manganese in molten steel which mainly occurs in the early period of converter smelting at a lower temperature, bottom blowing hydrogen can provide an amount of heat that makes the melt temperature increase more rapidly and shortens the oxidation time of manganese. As such, hydrogen blowing may have a positive effect on the manganese retention in steel.

On the other hand, there is a selective oxidation reaction between [Mn] and [C] in converter steelmaking, i.e., [C] + (MnO) = [Mn] + CO(g). When hydrogen is injected into the melts from the converter bottom at a high flow rate, a large number of hydrogen bubbles are generated. The partial pressure of CO in the dispersed hydrogen bubbles is very low, which can obviously improve the thermodynamic and kinetic conditions for the reaction. Thus, hydrogen bottom blowing can promote the reaction between carbon and oxygen and further play a certain role in decarburization and manganese preservation.

### 3.3.3. Effect of Hydrogen on Dephosphorization of Molten Steel

In converter smelting, [P] is removed from the molten steel by the reaction 2[P] + 5(FeO) + (CaO) = (CaO·$P_2O_5$) + 5[Fe] in molecular theory or 2[P] + 5($Fe^{2+}$) + 8($O^{2-}$) = 2($PO_4^{3-}$) + 5[Fe] in ionic theory. Both theories indicate that [P] is oxidized in the interface of molten steel and slag by the components of (FeO) and (CaO) or ions of ($Fe^{2+}$) and ($O^{2-}$) and is not directly oxidized by [O] in molten steel.

Hydrogen bottom blowing reduces the [O] in molten steel, as analyzed in 3.1. Will this have a detrimental effect on the removal of [P] from molten steel? According to the above analysis, the [O] in molten steel does not directly participate in the oxidation of [P] and thus has no direct detrimental effect on the removal of [P] from molten steel. On the other hand, [P] is mainly oxidized and removed from the steel in the early stage of steelmaking, while during that period, the reduction in [O] by hydrogen is relatively tiny compared with that in the middle and late period, as illustrated in Figure 7. Therefore, the reduction in [O] caused by hydrogen bottom blowing has no detrimental effect on the dephosphorization of molten steel.

Of course, the analysis in 3.2.1 shows that hydrogen can react with slag (FeO) in the middle and later stages of converter smelting, which is not beneficial to the dephosphorization reaction 2[P] + 5(FeO) + (CaO) = (CaO·$P_2O_5$) + 5[Fe] or 2[P] + 5($Fe^{2+}$) + 8($O^{2-}$) = 2($PO_4^{3-}$) + 5[Fe] in thermodynamics, and may aggravate the rephosphorization reaction in the later stages of converter steelmaking. However, as the content of (FeO) in slag is high, the reduction in the content of (FeO) in slag by hydrogen is limited, and the negative effect of hydrogen on dephosphorization in this way is limited.

However, the analysis in 3.2.4 shows that hydrogen tends to promote the dephosphorization of slag rather than the rephosphorization of molten steel in the late period of converter smelting. With the reduction in ($P_2O_5$) in slag, the dephosphorization reaction of 2[P] + 5(FeO) + (CaO) = (CaO·$P_2O_5$) + 5[Fe] or 2[P] + 5($Fe^{2+}$) + 8($O^{2-}$) = 2($PO_4^{3-}$) + 5[Fe] is promoted toward the right side, which is beneficial to dephosphorization, especially in the middle and later stages of converter smelting, and can inhibit rephosphorization in later stages.

On the other hand, a large number of studies have shown that intensive bottom blowing stirring is conducive to promoting the reactions of steel and slag, especially dephosphorization in converter steelmaking. Therefore, based on the comprehensive analysis of the above results, the intensive hydrogen bottom blowing proposed in this paper benefits dephosphorization in converter steelmaking.

### *3.4. Analyzation with FactSage Simulation*

In order to verify the correctness of the above thermodynamic calculation, FactSage software was used to analyze the variations in the components in the converter in different processes. Referring to the actual production data of the argon bottom blowing converter in Pangang Group Xichang Steel & Vanadium Co. Ltd, for every 100 kg of hot metal charged into the converter, 12.88 kg of scrap and 2 kg of slag former should be charged in the melting process. The compositions of the hot metal and scrap are shown in Table 1. The composition of the slag former is 55% of CaO, 25% of FeO, and 20% of $SiO_2$. The intensity of the oxygen top blowing and hydrogen bottom blowing were set to 3.33 $m^3 \cdot min^{-1} \cdot t^{-1}$ and 0.5 $m^3 \cdot min^{-1} \cdot t^{-1}$, respectively. The above parameters were input into FactSage to calculate the mass of each component in the argon bottom blowing converter and hydrogen bottom blowing converter during the middle period (9 min, 1417 °C) and late period (17 min, 1663 °C) of smelting. Some calculation results are shown in Tables 15 and 16.

**Table 15.** Mass of some components in middle periods of the two types steelmaking processes (kg).

| **Components**<br>**Process** | **[C]** | **[O]** | **[Fe]** | **[Mn]** | **[P]** |
|---|---|---|---|---|---|
| Argon bottom blowing | 1.7479 | $7.6898 \times 10^{-4}$ | 107.66 | $2.4456 \times 10^{-2}$ | $5.99 \times 10^{-2}$ |
| Hydrogen bottom blowing | 1.7487 | $7.1403 \times 10^{-4}$ | 107.66 | $2.4454 \times 10^{-2}$ | $5.99 \times 10^{-2}$ |

**Table 16.** Mass of some components in late periods of the two types steelmaking processes (kg).

| **Components**<br>**Process** | **[C]** | **[O]** | **[Fe]** | **[Mn]** | **[P]** | **Fe in slag** | **($P_2O_5$)** |
|---|---|---|---|---|---|---|---|
| Argon bottom blowing | $1.0312 \times 10^{-2}$ | 0.19404 | 105.97 | $3.3118 \times 10^{-3}$ | $5.9784 \times 10^{-2}$ | 1.6886 | $2.2353 \times 10^{-4}$ |
| Hydrogen bottom blowing | $1.0735 \times 10^{-2}$ | 0.17347 | 106.27 | $3.9603 \times 10^{-3}$ | $5.9827 \times 10^{-2}$ | 1.3867 | $1.2812 \times 10^{-4}$ |

The reactions in actual converter steelmaking are limited by heat and mass transfer, and it is impossible for the components in the converter to reach an equilibrium composition in the short smelting time. However, FactSage simulations can calculate the equilibrium compositions of each component in various steelmaking processes and provide a reference for judging the possibilities and degrees of the reactions.

According to Tables 15 and 16, when the reactions in the converter reach equilibrium during the middle period of smelting, bottom blowing hydrogen or argon has almost no effect on the content of [C] in the molten steel, while in the later period of smelting, compared with the argon bottom blowing converter, the mass of [C] in the molten steel of the hydrogen bottom blowing converter rises from $1.0312 \times 10^{-2}$ kg to $1.0735 \times 10^{-2}$ kg, with an increment of 4.10%. This indicates that hydrogen blowing has little effect on the content of [C] in molten steel in the early and middle periods, but can inhibit the rapid decrease in [C] during the later period and is beneficial for controlling the [C] content of molten steel at the endpoint. This matches the analysis in 3.3.1.

During the middle period of smelting, compared with the argon bottom blowing converter, the content of [O] in the molten steel of the hydrogen bottom blowing converter decreases from $7.4898 \times 10^{-4}$ kg to $7.1403 \times 10^{-4}$ kg, with a negligible drop of $3.5 \times 10^{-5}$ kg. During the later period, however, the [O] content in molten steel in the bottom blowing hydrogen converter decreases from 0.19404 kg to 0.17347 kg, with a remarkable decrease of 0.02 kg and 10.60%. This indicates that hydrogen blowing has little effect on the content of [O] in molten steel during the early and middle periods, however, it can inhibit the rapid increase in [O] during the late stage and further control the carbon–oxygen reaction rate. This matches the analysis in 3.1.

During the late period of smelting, the mass of [Fe] in the molten steel in the hydrogen bottom blowing converter increases to 106.27 kg compared with 105.97 kg in the Ar bottom blowing converter. At the same time, the mass of Fe element in the slag (including Fe in FeO, $Fe_2O_3$, FeS, and other compounds) decreases from 1.6886 kg to 1.3867 kg by 17.88%.

This shows that hydrogen bottom blowing can reduce (FeO) in slag and reduce the iron loss in the late period of smelting, which is consistent with the discussion in Section 3.2.1.

During the middle period of smelting, hydrogen bottom blowing has almost no effect on the content of [Mn] in molten steel. However, during the late period, the content of [Mn] in molten steel increased from $3.3118 \times 10^{-3}$ kg to $3.9603 \times 10^{-3}$ kg, with an increment of 19.58%. This is consistent with the analysis in Sections 3.2.3 and 3.3.2

During the late period of smelting, hydrogen bottom blowing increases the [P] in the molten steel from 5.9784 kg to 5.9827 kg, a negligible increment of 0.07%. In contrast, the mass of ($P_2O_5$) in the slag decreases from $2.2353 \times 10^{-4}$ kg to $1.2812 \times 10^{-4}$ kg, a remarkable reduction rate of 42.68%. This shows that hydrogen bottom blowing can promote the gasification dephosphorization of slag, which is consistent with the analysis in 3.2.4.

In sum, the calculation results of FactSage are in good agreement with the results of the above thermodynamic calculation. The potential roles of $CO_2$ emission reduction and the reduction of [O], (FeO), and (MnO) in traditional top–bottom blowing converter melting by application of hydrogen bottom blowing are practicable.

## 4. Conclusions

1. In reference to the process of converter steelmaking in Pangang Group Xichang Steel & Vanadium Co. Ltd, hydrogen bottom blowing at intensities of 0.1–0.5 $m^3 \cdot min^{-1} \cdot t^{-1}$ instead of traditional argon bottom blowing can increase the scrap/hot metal charging ratio by 0.89%–3.80% and reduce $CO_2$ emissions by 19.79–84.95 $kg \cdot t^{-1}$. As for preheated scrap, the increase in scrap ratio is 1.23–5.19% and the $CO_2$ emission reduction is 27.44–115.96 $kg \cdot t^{-1}$. Keeping the scrap ratio unchanged, the temperature of the melts increases by 16–73 K with hydrogen bottom blowing.
2. Hydrogen can play a restraining role on the rapidly increasing oxygen content at the end of steelmaking, and is helpful in controlling the endpoint of converter steelmaking. Hydrogen bottom blowing has little effect on [O] in molten steel during the early and middle steelmaking periods. However, during the late period of smelting, hydrogen significantly reacts with [O] in molten steel, and the equilibrium partial pressure ratio of water and hydrogen for the reaction is high.
3. Hydrogen can reduce (FeO) in slag to a certain extent during the middle and later stages of converter smelting, which is beneficial to the oxibility controlling of slag and the reduction in the iron loss in steelmaking.
4. In the early and middle periods of steelmaking, the effect of hydrogen on the decarbonization reaction is very tiny. However, during the late period, when the conjugate reaction $H_2 + CO = [C] + H_2O$ reaches equilibrium, 8.80% of hydrogen in the bubbles react with water. The reducibility of hydrogen is beneficial to delaying the excessively rapid oxidation of carbon and controlling the carbon content at the endpoint of converter smelting.
5. Hydrogen tends to promote the gasification dephosphorization of slag rather than the dephosphorization of molten steel, and the dephosphorization is slight. Meanwhile, hydrogen may achieve the purpose of manganese preservation by inhibiting the increase in dissolved oxygen content in molten steel, increasing the converter temperature during the early period of smelting, and controlling the selective oxidation reaction between [Mn] and [C].

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