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Application of Spectroscopic Analysis Techniques to the Determination of Slag Structures and Properties: Effect of Water Vapor on Slag Chemistry Relevant to a Novel Flash Ironmaking Technology

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Flash ironmaking technology is an ecofriendly process for producing iron from iron oxide concentrates via a flash reactor that uses gaseous fuels and reductants that reduce energy consumption and minimize greenhouse gas emissions. It has the potential to achieve steelmaking in a single, continuous process. The phase equilibria and chemistry of selected slag systems were investigated during the development of a novel flash ironmaking process. Among the proposed reductants and fuels are H_2, natural gas, and coal gas. In different ironmaking processes, the molten bath (iron-slag bath) is expected to be at equilibrium with gas atmospheres of H_2/H_2O, $CO/CO_2/H_2/H_2O$, and CO/CO_2. The first two gas mixtures were used to represent the processes based on H_2 or natural gas/coal gas, respectively, whereas the CO/CO_2 mixture was used for a comparison. The slag composition of interest in this process was selected to resemble that of the blast furnace and is based on the CaO-MgO-SiO_2-Al_2O_3-FeO-MnO-P_2O_5 system with CaO/SiO_2 in the range 0.8–1.4. The temperature range was 1550–1650°C encompassing a wide range of expected ironmaking temperatures for the novel flash process. The oxygen partial pressure was maintained in the reducing range of 10^{-10}–10^{-9} atm in the three gas atmospheres. It was found that H_2O dramatically affects the chemistry of the slag and strongly affects the phase equilibria in the slag as well as the equilibrium distribution of elements between slag and molten metal. The effects of water vapor on the chemistry of the slag as well as the equilibrium reactions involving the slag have been studied for the first time.

INTRODUCTION

Given the issues related to large carbon dioxide emissions and energy consumption in the best existing ironmaking technologies, a novel flash ironmaking technology was conceived by Sohn and coworkers[1–3] at the University of Utah. This technology is based on the direct gaseous reduction of iron ore concentrate particles using natural gas, hydrogen, coal gas, or a combination thereof. It is the first ironmaking process converting iron ore concentrate directly to metallic iron in-flight that would be suitable for an industrial-scale operation. This process will produce iron directly from concentrate without requiring pelletization or sintering and avoid the need for coke. In addition, this process concept takes full advantage of the fine particle size of concentrate with a large surface area, which permits rapid reduction by a gas. Another potential benefit of this process is the possibility of direct steelmaking in a single continuous process, as shown in Fig. 1.[4] Kinetic feasibility tests on the reduction of magnetite concentrate particles by hydrogen have been carried out in the temperature range 1150–1400°C.[5–7] Most importantly, these tests have revealed that high reduction degrees above 90% can be achieved within the several seconds of residence time available in a flash reactor. In addition to the kinetics study, process simulation for the flash ironmaking process has been carried

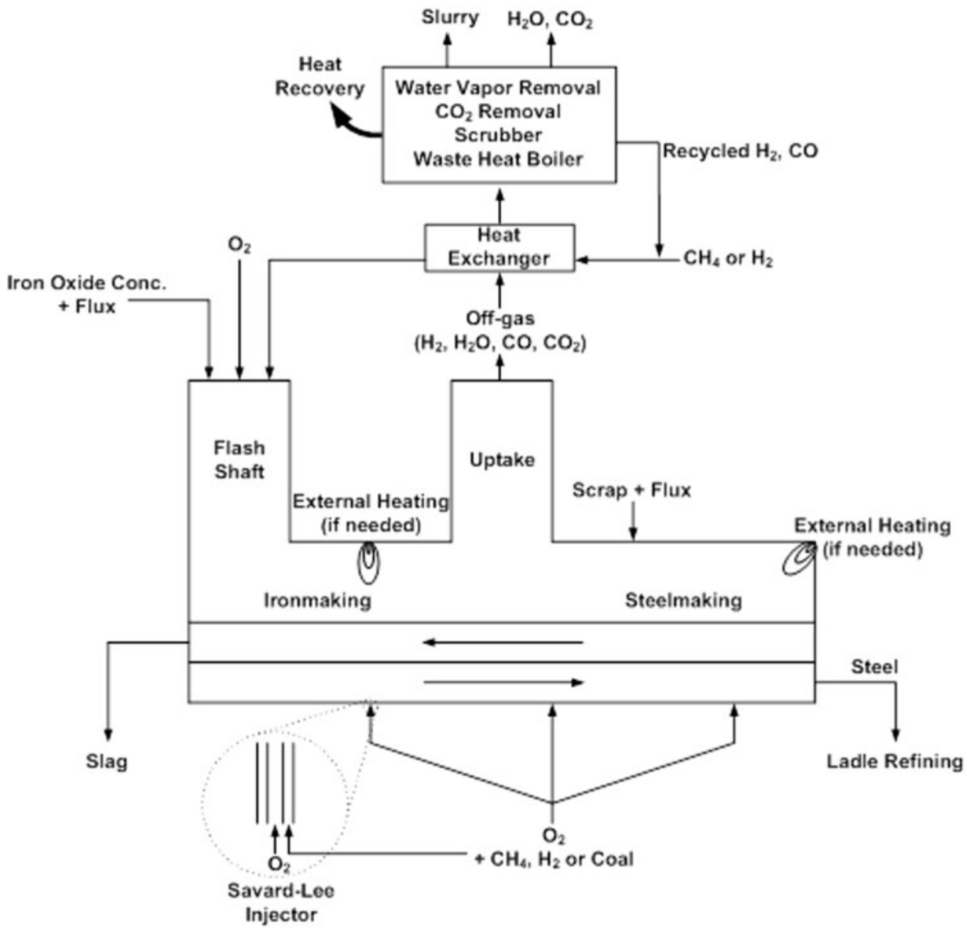

Fig. 1. A schematic diagram of the novel flash process.[4]

out to assess the energy requirement, carbon dioxide emissions, and the economic feasibility using different process configurations.[8–11] The major results are summarized in Fig. 2, in which the first five cases show the values for different possible modes of operation of the new technology. The last case is for an average blast furnace operation, for which only energy consumption and carbon dioxide values are presented. Furthermore, when comparing the values for the novel technology with those for the blast furnace, it should be recognized that the latter is a proven technology, whereas the former is still under development and thus carries a considerable risk factor.

Currently, the novel flash process is undergoing large bench-scale testing to investigate different process variables using natural gas as the fuel and reductant. Because the effects of an H_2O-containing atmosphere on slag properties have not been studied before, it is critical for the development of the novel flash process to determine these effects.

EXPERIMENTAL WORK

A CaO-MgO-SiO_2-Al_2O_3-FeO-MnO (<1.0 wt%)-P_2O_5 (<0.5 wt%) slag was used in the study. The major components of the slag were chosen to simulate that of a typical ironmaking process, as listed in Table I.

The experimental temperature range was 1550–1650°C, which is wide enough to encompass the expected operating temperatures of the novel ironmaking process. Equilibrium experiments were conducted under $CO/CO_2/H_2/H_2O$, H_2/H_2O and CO/CO_2 atmospheres. The first gas mixture was used to represent the conditions of using natural gas or coal gas in the reduction process, whereas the second mixture was used to represent the case of using pure H_2 gas. It is noted that although CO/CO_2 mixtures in the similar pO_2 range were tested for comparison, this does not closely represent the blast furnace conditions in which the 4 wt% C to 5 wt% C[12] in iron in the hearth makes pO_2 at the interface between molten iron and the slag much lower (10^{-15}–10^{-14} atm)[13–16] than the 10^{-10}–10^{-9} atm range expected in the new flash ironmaking process. Thus, the FeO content in the blast furnace slag is expected to be accordingly lower at around 1%.

Mixtures of dry powders of SiO_2, Al_2O_3, and MgO were premelted at 1600°C for homogeneity. Water was injected as a liquid using a MASTERFLEX digital peristaltic pump drive (Cole-Parmer

Instrument, Vernon Hills, IL), which provided flow rates from 0.001 mL/min to 3400 mL/min (with the aid of 10 different size pump tubings) using the same brand pump head with an accuracy of ±0.1% of the flow rate.

The temperature and oxygen partial pressure ranges were chosen to be 1550–1650°C and 10^{-10}–10^{-9} atm, respectively, which were wide enough to encompass the expected operating temperature of the new process based on the hydrogen or natural gas reduction of iron ore concentrate.

The samples were prepared as 2.5 g and 1.0 g of slag mixed with 2.5 g and 1.0 g of iron powder, respectively, for experiments under H_2/H_2O and the comparison experiments under the three gas atmospheres.

The composition of the slag phase was analyzed by inductively coupled plasma-optical emission spectroscopy. Other details of the experimental procedure have been discussed in detail elsewhere.[17–19]

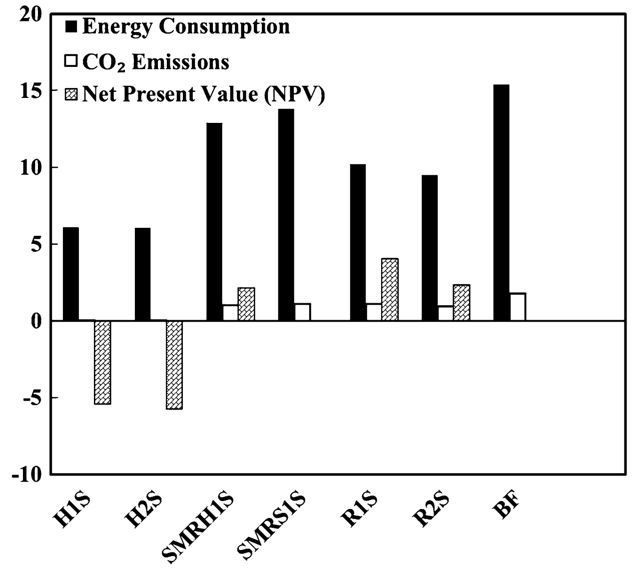

Fig. 2. Energy consumption (GJ/ton of iron), CO_2 emission (tons/ton of iron), and NPV (in 2010 dollars and conditions) in million dollars for a 1 Mt/year plant of the different configurations of the flash ironmaking process in addition to the blast furnace applying \$0 CO_2 credit. (H1S: H_2-based 1-step process, H2S: H_2-based 2-step process, SMRH1S: 1-step process with hydrogen production from SMR (Steam-Methane Reforming), SMRS1S: 1-step process with syngas production from SMR, R1S: Reformerless 1-step process, R2S: Reformerless 2-step process).[8–11]

To determine the effect of gas composition on the chemistry of the slag, three sets of experiments were conducted under the following conditions:

1. Initial (before MgO presaturation) slag composition (in wt%) was the same in the three experiments [CaO (29), SiO_2 (29), MgO (10), Al_2O_3 (15), MnO (2), FeO (15), FeS (0.9), $Ca_2P_2O_7$ (1.5), CaO/SiO_2 = 1.0].
2. pO_2 was $\sim 1.5 \times 10^{-10}$ atm in the three experiments that were controlled by CO/CO_2, H_2/H_2O, and $H_2/H_2O/CO/CO_2$.
3. Temperature was controlled in the range of 1550–1650°C.

Quenching preserves the majority of the chemical and structural properties of molten slag.[20] Therefore, several techniques such as vibration spectroscopic techniques, x-ray emission spectroscopy, and x-ray diffraction (XRD) were used to investigate the structure of slags after quenching. Vibrational excitations in the slag samples can be studied in the infrared (IR) and the visible spectrum region via IR and Raman spectroscopy, respectively. Raman spectroscopy has been used extensively in slag and molten silicates research because the detection methods for the visible region are well developed. Many of the recent advances in the slag structure field have come from research on magmas and natural minerals done by geological laboratories.[20]

In this study, Fourier transform IR-reflection absorption spectroscopy (FTIR-RAS), Raman spectroscopy, and x-ray photon spectroscopy, XRD, and scanning electron microscope equipped with energy-dispersive spectrometer were adopted to explore the effect of gas composition on the chemistry of the ironmaking slag. Additional details have been discussed elsewhere.[19]

RESULTS AND DISCUSSIONS

The Chemistry of the Slag

Figure 3 presents the FTIR spectra of three identical slag samples under different gas atmospheres at 1550°C. Although the temperature, slag compositions, and oxygen partial pressure were held the same for the three slags, it is clear that

Table I. The starting slag composition in weight percent

Slag	CaO	SiO_2	MgO	Al_2O_3	MnO	FeO	FeS	$Ca_2P_2O_7$	CaO/SiO_2
1	29	36	10	10	0	14	0.3	0.3	0.8
2	33	33	10	10	0	14	0.3	0.3	1
3	35	30	10	10	0	14	0.3	0.3	1.2
4	38	27	10	10	0	14	0.3	0.3	1.4
5	26	32	10	15	2	13	0.9	1.5	0.8
6	29	29	10	15	2	13	0.9	1.5	1
7	32	26	10	15	2	13	0.9	1.5	1.2

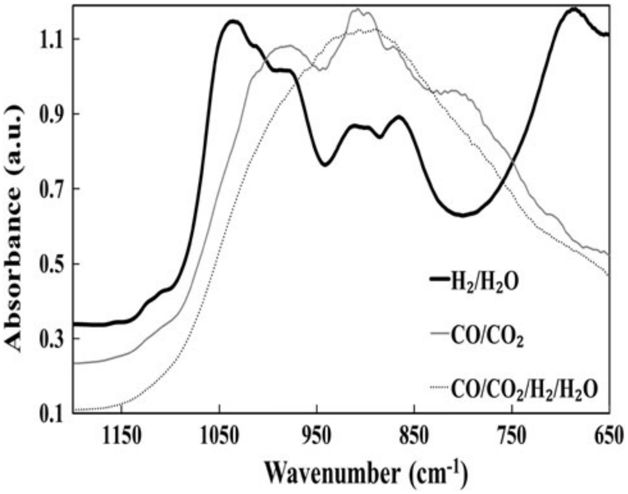

Fig. 3. FTIR-RAS spectra under the three different gas mixtures.

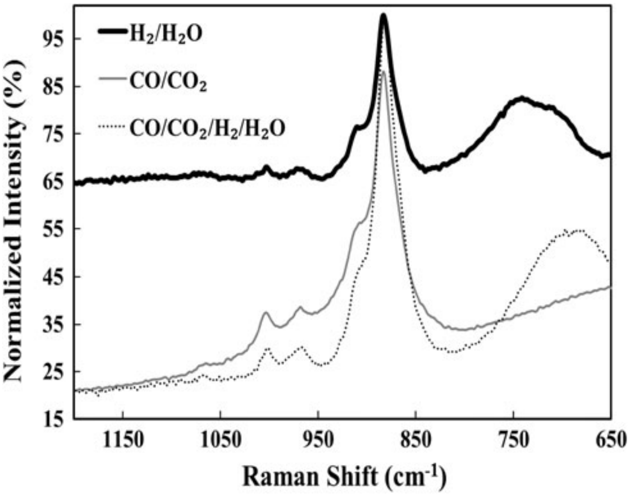

Fig. 4. Raman spectra under the three different gas mixtures.

there are distinct peaks associated with each gas mixture. This is also apparent in the Raman spectra, as shown in Fig. 4. In addition, XRD shows that the intensity of the fayalite peak decreases with an increase in pH_2O, as can be seen in Fig. 5.

In this article, we introduce the main features of the application of spectroscopic techniques to the analysis of slag structures. The identification of each peak requires deconvolution of the overlapping broad spectra, which is a complex process. For more details, the reader is referred to Ref. 19. Based on the spectroscopic and XRD analyses in addition to nonbridging oxygen per tetrahedra (NBO/T; the higher this ratio the lower the polymerization degree) calculations, H_2O stabilizes the more polymerized silicates anions rather than the depolymerized monomers. It was found that at 1550°C, the slags under H_2 and natural gas/coal gas (NG/CG) exhibit BO (bridging oxygen; the higher the BO, the higher the polymerization degree) of 55 and 9% more than under CO/CO_2, whereas the ratio NBO/T of both showed ~35% less than under CO/CO_2. Therefore, it can be concluded that the higher the water content in the gas atmosphere, the more polymerized the silicates in the slag. In the following sections, the effect of this phenomenon on the quality of the produced iron, the loss of iron in the form of FeO, and MgO solubility will be summarized.

The representative results were based on the average obtained using slag MgO-saturated CaO-FeO-Al_2O_3-SiO_2-MnO (0.2–0.8 wt%)-P_2O_5 (0.1–0.9 wt%), at 1550°C, under $pO_2 = 2 \times 10^{-10}$ atm with CaO/SiO_2 range 0.8–1.2. These conditions are expected to be closest to an industrial operation of this novel flash ironmaking process under development. The trend of the studied properties was similar regardless of the value of CaO/SiO_2; therefore, representative graphs at CaO/SiO_2 of only 1.2 were presented in this article as an example of a comprehensive set of results. The comparisons are based on an ore with materials balance using iron ore with approximately 0.02 wt%, 0.6 wt%, and 0.2 wt% S, P, and Mn, respectively, in addition to coke (in the blast furnace) having average contents of 0.9 wt%, 0.03 wt%, and 0.07 wt% S, P, and Mn, respectively. The coke-to-metal ratio used in the case of the blast furnace was 0.4. In addition to the difference in S input between the novel flash process and the blast furnace, another important difference is the volatilization of ~30 wt% and 25 wt% S and P during the downward flight of the particles in the reactor shaft in the latter process, which was also considered in the calculations. The same slag/metal weight ratio was 0.3 in all the three routes.

Sulfur Distribution Ratio (L_S)

H_2/H_2O showed 500% ($L_S = 4.0$) enhancement in L_S, whereas NG/CG exhibited 250% (2.0) improvement compared with CO/CO_2 (0.8). Figure 6 shows that L_S increases with pH_2O for the same slag composition regardless of temperature.

Phosphorus Distribution Ratio (L_P)

Under H_2/H_2O ($L_P = 8.0$) and NG/CG ($L_P = 17.0$), L_P was 60% and 15% less than under CO/CO_2 (20), respectively. Based on materials balance calculations, the hot metal produced by H_2 ([wt% P] = 0.11) and NG/CG (0.06) would have similar and 55% less P compared with CO/CO_2 (0.11). Figure 7 presents the influence of pH_2O on L_P for the same slag composition at various temperatures. It is seen that L_P decreases as pH_2O increases. The typical pig iron has ~0.2 wt% P. Therefore, the novel flash process is expected to produce iron with less need for dephosphorization in the steelmaking step.

Manganese Distribution Ratio (L_{Mn})

Water in the gas atmosphere depresses L_{Mn}. It was found that L_{Mn} under H_2 ($L_{Mn} = 5.0$) and NG/

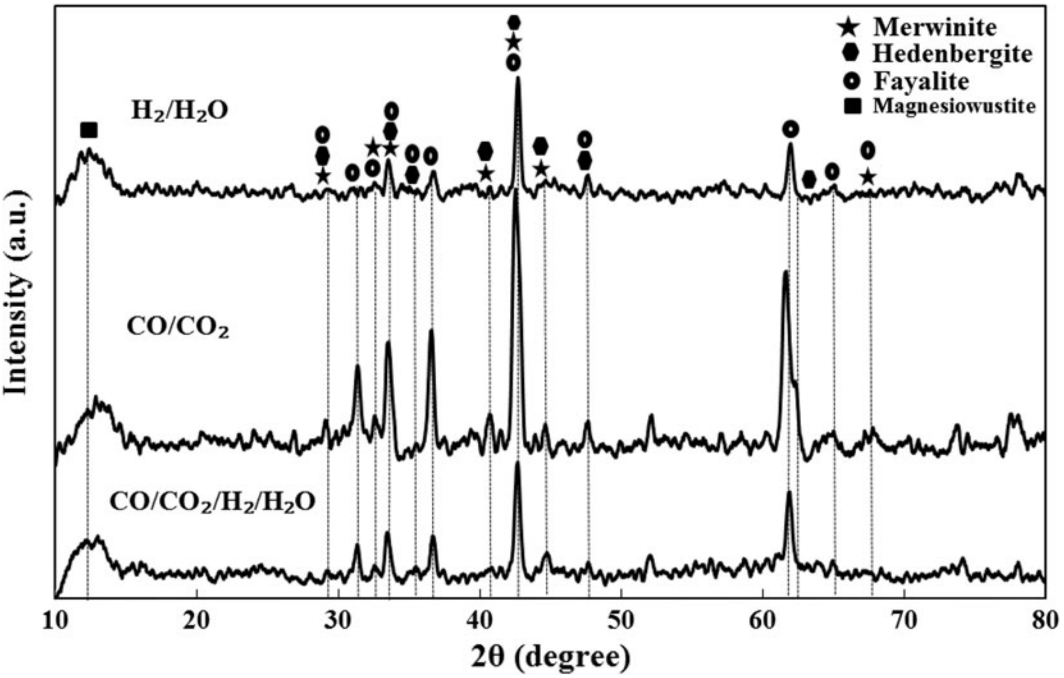

Fig. 5. XRD patterns of slag under the three different gas mixtures.

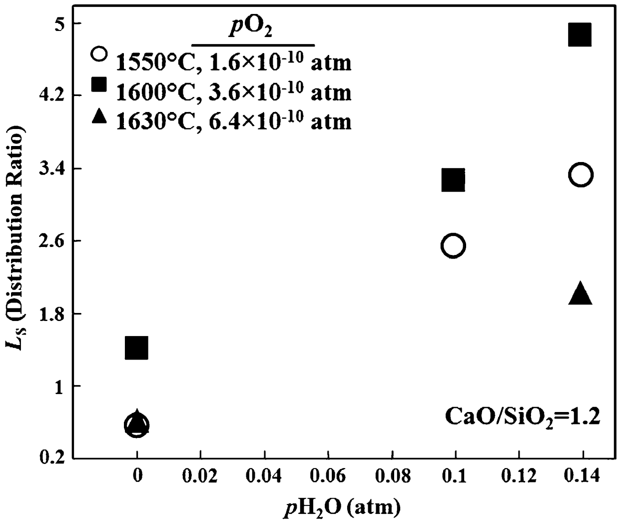

Fig. 6. Effect of pH_2O on L_S at wt% CaO/wt% SiO_2 of 1.2 at different temperatures and pO_2.

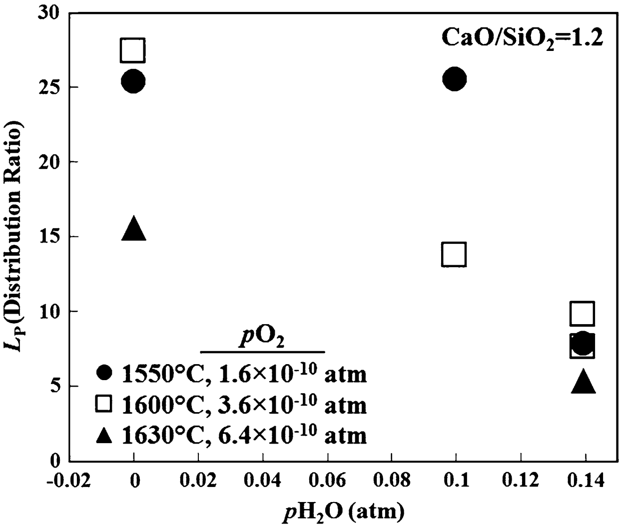

Fig. 7. Effect of pH_2O on L_P for slag compositions with wt% CaO/ wt% SiO_2 of 1.2 at various temperatures and pO_2.

CG (L_{Mn} = 6.0) is comparable to that under CO/CO_2 (L_{Mn} = 5.0). In other words, if the same ore is fed into three routes and by applying material balance, then H_2 (0.11 wt% Mn) and NG/CG (0.10 wt% Mn) are expected to produce iron with 8% and 17% less Mn than CO/CO_2 (0.12 wt% Mn). Figure 8 presents the effect of water content in the gas on L_{Mn} for slags with the same composition at different temperatures and pO_2. It shows that water in the gas atmosphere suppresses L_{Mn}. The typical pig iron has a Mn content of 0.9–2.5 wt%, and hence, the novel flash process is anticipated to produce iron with a lower Mn content than the blast furnace from the same raw materials.

FeO Content and MgO Solubility in the Slag

One of the advantages of the H_2O in the gas atmosphere is that it increases the activity coefficient of FeO in the slag and accordingly lowers the FeO content. It was found that the FeO content in the slag under H_2 (FeO wt% = 10) and NG/CG (FeO wt% = 10) is 62% less than under CO/CO_2 (FeO wt% = 26). In the typical blast furnace process, the FeO content in the

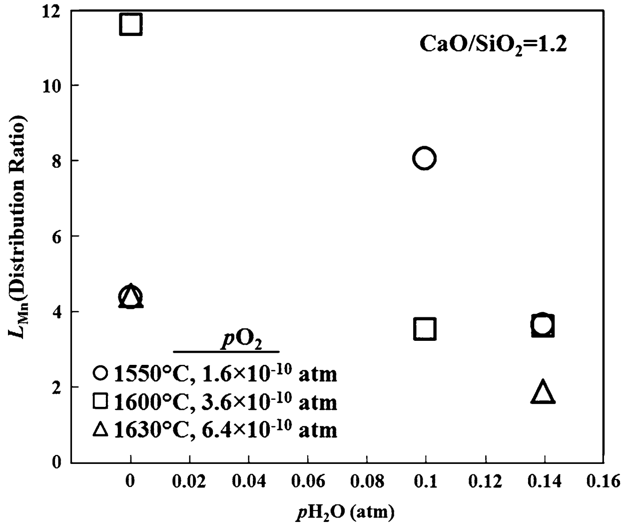

Fig. 8. Effect of water content in the gas on L_{Mn} at wt% CaO/wt% SiO$_2$ of 1.2 at different temperatures and pO$_2$.

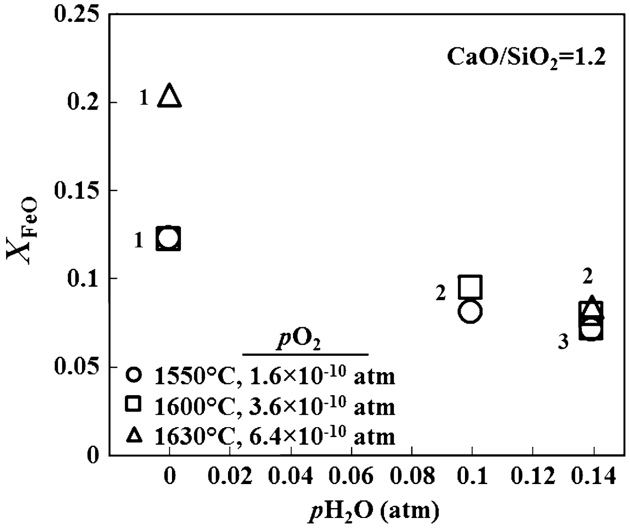

Fig. 9. Effect of pH$_2$O on X_{FeO} for slags with wt% CaO/wt% SiO$_2$ of 1.2 at different temperatures and pO$_2$.

slag is ~1 wt% due to the lower pO_2 because of the carbon content in hot metal as mentioned earlier. Figure 9 exhibits the FeO content in the slag as a function of water content in the gas atmosphere. It is indicated that water helps decrease the FeO content in the slag.

The MgO solubility at 1550°C and pO_2 of 2×10^{-10} atm and CaO/SiO$_2$ of 1.0, was 17 wt%, 20 wt%, and 26 wt%, respectively, for slags under NG/CG, H_2, and CO/CO$_2$ atmospheres. Therefore, water vapor would decrease lining wear, as MgO solubility in slag under H_2O-containing atmospheres is substantially smaller than that under the CO/CO$_2$ atmosphere. (Despite this apparent advantage, potential safety concerns associated with the use of hydrogen-containing gases in the new process must be recognized and carefully taken into consideration in the design and operation of the facility.) It is noted that MgO solubility in slag shows a small increase with increasing pH_2O beyond ironmaking conditions, as shown in Fig. 10.

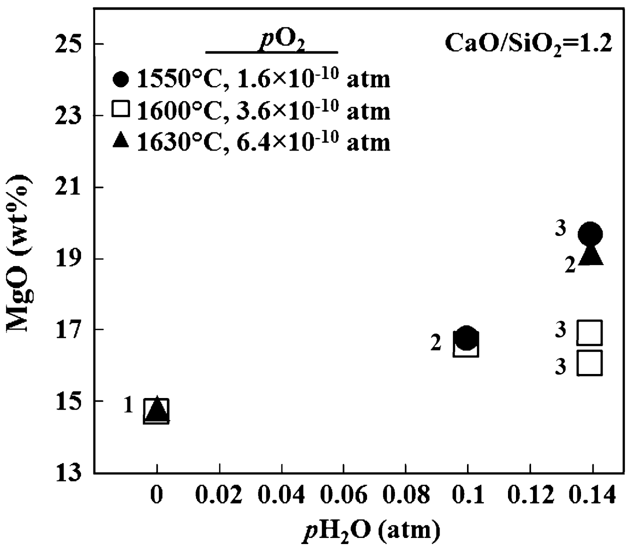

Fig. 10. Effect of water content in the gas on MgO solubility at wt% CaO/wt% SiO$_2$ of 1.2 at different temperatures and pO$_2$.

CONCLUSIONS

A number of analytical techniques were applied to the determination of the structures and properties of slags. These techniques have been proven to be highly useful for this purpose. Several features of such instrumental analysis have direct correlations with important properties of slag such as its affinity to impurities.

These analytical techniques were applied to slags of interest for a novel flash ironmaking process, especially in terms of the effects of water vapor expected to be present in high contents in the new process. Water vapor was found to be advantageous in terms of lowering FeO uptake in the slag in the novel flash ironmaking. Water can also be expected to decrease the sulfur, phosphorus, and manganese content in the iron produced by the flash ironmaking process. In addition, it was determined that water vapor in the atmosphere of the new process would keep lining wear low based on the low MgO solubility in slag under its expected operating conditions. Thus, based on the results of this work, water was found to have pronounced effects on the chemistry of the slag as well as the important equilibrium reactions relevant to ironmaking. This research is the first in the field to study the effect of water vapor on the slag–metal equilibria. This research answered important questions about the novel flash ironmaking process, such as the quality of the produced iron, the iron loss into the slag, and the lining erosion.

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DISCLAIMER

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