Development of H_2 Production Process with Utilization of Steelmaking Slag

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Abstract: The amount of CO_2 emitted from steelmaking industry occupies approximately 13 % of total CO_2 emission in Japan, and thus the development of environmental-friendly ironmaking and steelmaking processes is one of the urgent issues. Currently, most of by-products such as slags, gas, dust and so on, are efficiently utilized as much as possible. However, the heat which many by-products have at high temperatures at discharge from the processes is not utilized completely, and especially the heat associated with the slags is not utilized at all. The amount of waste heat from converter slag is estimated to be 2.4×10^{16} J, which is equivalent to the annual energy consumption of 570,000 families in Japan. Therefore, this unharnessed energy should be efficiently recovered and utilized in steelmaking industry or in society for the reduction of total energy consumption and CO_2 emission. Converter slag contains 15 to 30 mass% of FeO normally, and thus the function of FeO as a reducing agent of H_2O gas is expected; 2FeO (in slag) + H_2O (g) = Fe_2O_3 (in slag) + H_2 (g). Since the above reaction is exothermic, the supply of heat energy for operation of this process would be unnecessary, or only a little heat supply would be required. Therefore, the necessary heat energy could be supplied via discharged converter slag at molten state. The ultimate target of this research is to develop the new H_2 production process by utilizing unused thermal and chemical energy of converter slag without any other energy supply. In the present study, our recent researches regarding development of H_2 production process with steelmaking slag were reviewed; firstly the simulation of thermodynamic conditions required for process operation and secondly the measurement of kinetics of the production of H_2 gas from water vapor by converter slag containing FeO by laboratory-scale experiments. The equilibrium between Ar–H_2O gas and CaO–FeO–SiO_2 slag was calculated with various conditions in composition and temperature. The produced amount of H_2 gas increased with increasing initial slag and gas temperature, the partial pressure of H_2O, and FeO content of slag. The slag weight increased by blowing Ar–H_2O gas and FeO was oxidized to Fe_2O_3. The exhaust gas analysis by a quadrupole mass spectrometer confirmed the generation of H_2 gas.

Key words: ironmaking, steelmaking, green energy, water vapor, slag utilization

1. Introduction

Iron and steelmaking process via blast furnace – converter process from iron ore is an essential steel production route for Japanese steel industries to stably supply high quality steel products in large quantity to society. Blast furnace – converter process consumes huge amount of fossil fuels such as mainly coal, resulting the emission of considerable amount of CO_2 gas. Since the emission of CO_2 gas from steel industries accounts for approximately 12 % of domestic CO_2 gas emission in Japan (FY2009),[1] it is an urgent issue to develop environmental-friendly ironmaking and steelmaking processes and reduce CO_2 emission for steel industries.

Various kinds of gases and by-products generated from ironmaking and steelmaking processes are recycled as much as possible at present. Enormous thermal energy is also generated from processes and released to surrounding atmosphere as various forms such as sensible heats of gases, molten steels or by-products, and as heat losses. However, these energies are not utilized before final dissipation to atmosphere. Although various technologies to utilize thermal energy from ironmaking and steelmaking processes have been attempted to develop, practical application of these technologies has not been achieved because the thermal energy is not always useful as an energy source.

In steelmaking process by converter, fluxing agent such as CaO is added during reefing and about 100 kg/t-steel of steelmaking slag are generated. Since the steelmaking slag is discharged at temperature range between 1873 and 1923 K after discharge of refined molten steel, it has large thermal energy. Amount of generated steelmaking slag is 11.7 Mt/y (FY2010) in Japan.[2] Assuming the amount of steelmaking slag is 10 Mt/y and its heat capacity from room temperature to 1923 K is 1 J/g·K,[3] unutilized heat is estimated to be 16 PJ, which is equal to annual energy consumption of 420 thousand families in Japan.[4]

Since steelmaking slag contains relatively large concentration of FeO in the range from 20 to 30 mass%, reduction of H_2O gas by FeO described as reaction (1) is expected,

$$2\ \mathrm{FeO\ (l)} + \mathrm{H_2O\ (g)} = \mathrm{Fe_2O_3\ (s)} + \mathrm{H_2\ (g)} \qquad \Delta G^\circ = -82130 + 102.7T\ \mathrm{J/mol}\ [5] \qquad (1)$$

From Gibbs free energy change of reaction (1), this reaction does not proceed forward spontaneously in standards states of reactants and products, and progress of the reaction to equilibrium is expected. In addition, no heat or only small heat supply may be necessary because reaction (1) is exothermic, and thus it is considered that thermal energy required for stable operation could be supplied sufficiently by sensible heat of converter slag. From above reasons, the development of energy-saving H_2 production process without further energy consumption would be possible.

However, FeO and Fe_2O_3 contents in the slag decrease and increase, respectively, with progress of reaction (1). This compositional change results in the increment in solid fraction or viscosity of slag affecting the physical properties of slag such as fluidity and thus operational condition of H_2 gas production process. Accordingly, sufficient understanding of the physical chemistry of reaction between slag containing FeO and steam gas is important for precise operation of the process.

In this paper, our recent researches regarding development of H_2 production process with converter slag were reviewed; firstly the simulation of thermodynamics of the reaction between FeO–CaO–SiO_2 slag system and H_2O–Ar gas to examine the effects of temperatures, compositions of gas and slag on the behavior of H_2 gas production or the physicochemical properties of slag.[6] Secondly, the measurement of the generation behavior of H_2 gas by reaction between FeO-containing slag and H_2O–Ar gas at 1723 K to clarify the effect of slag compositions on the behavior of H_2 gas production.[7]

2. Thermodynamic Simulation for Reaction Between Steelmaking Slag and Water Vapor[6]

2.1 Conditions for Calculation

Thermodynamic calculation software FactSage 6.2 was used for estimation of equilibrium state between FeO-containing slag and H_2O-containing gas, and H_2 gas generation behavior.

Table 1 shows the detail of calculation conditions. Firstly, the initial condensed phases including molten slag and solid oxides were prepared by inputting oxide constituents with prescribed compositions and equilibrating at initial slag temperature. Subsequently the prepared condensed phases were equilibrated with H_2O–Ar gas. In the case of the preparation of initial condensed phases, FeO, CaO and SiO_2 were input to be 1 kg as a total, and then 56 kinds of pure compounds (pure liquid species: 7 and pure solid species: 49) and 12 kinds of solutions considering 39 species were considered in the equilibrium calculation as final candidates at predetermined temperature. In this stage, the formation of gas phase was not allowed. Non molten slag phases such as metallic or $2CaO{\cdot}SiO_2$ phase were formed in some calculations and these phases were also taken into account for slag-gas equilibrium calculation. In the slag-gas equilibrium calculation, 105 kinds of pure compounds (pure gaseous species in ideal behavior: 26, pure liquid species: 9 and pure solid species: 70) and 12 kinds of solutions considering 40 species were considered in the equilibrium calculation as final candidates. For the estimation of change in composition of condensed phases and system temperature with proceeding of reaction between slag and gas, 10 L of H_2O–Ar gas at predetermined gas temperature were equilibrated with condensed phases at the condition of no enthalpy change of the system at one calculation step. Condensed phases such as molten slag or various solids after equilibrium calculation were input as initial condensed phases in the next calculation, and 10 L of new H_2O–Ar gas were equilibrated again. The above equilibrium calculation between slag and gas were repeated by decreasing temperature less than 1722 K. Change in slag compositions and system temperature with process of reaction between slag and gas were estimated.

2.2 Simulation Results

One of calculation results are shown below to clarify the effects of initial FeO content of slag (from 10 to 40 mass%) and gas temperature (from 473 to 1273 K) with mass%CaO/mass%SiO_2 = 3, maintaining initial slag temperature = 1873 K, and partial pressure of H_2O in H_2O–Ar gas = 1.0 atm (no Ar gas).

Figure 1 shows the change in the amount of produced H_2 gas with volume of introduced H_2O gas. The amount of produced H_2 gas is here the accumulated amount of H_2 gas produced by repetitive slag-gas equilibrium calculation. Increase in introduced gas temperature increased the amount of produced H_2 gas in all calculation conditions, which is because temperature drop by equilibrium between gas and slag became smaller with increasing gas temperature and thus more H_2O gas could react with FeO contained in slag. Increase in initial FeO content in slag increased the amount of produced H_2 gas.

Figure 2 shows the change in solid fraction of slag phase with introduced gas volume. With larger initial FeO content, solid fraction decreases because the slag composition becomes closer to the liquidus, which is favorable to maintain the fluidity of slag for the stable operation.

Figure 3 shows the change in production ratio of H_2 gas with introduced H_2O gas volume, where production ratio of H_2 gas is defined as the molar ratio of the amount of generated H_2 gas to that of introduced 10 L H_2O–Ar gas in one equilibrium calculation. The effect of gas temperature or initial FeO content on the production ratio of H_2 gas is small.

The production ratio of H_2 gas is the largest at the beginning of reaction, from 60 to 85 %, and decreases much with increasing introduced gas volume.

Figure 4 shows the change in slag temperature with introduced gas volume. Although reaction (1) is exothermic, system temperature decreases with increasing introduced gas volume because temperature of the introduced gas is lower than that of slag and thus thermal energies of slag and generated heat by reaction (1) are flown out as sensible heat of exhaust gas. Slag temperature increases once after decreases at the initial stage, and then decreases again with increasing introduced gas volume. This transient temperature increase is due to the increase of solid fraction as shown in Fig. 2, because FeO in slag is oxidized by H_2O gas to Fe_2O_3 and liquidus temperature changes. In the present calculation conditions, temperature increases transiently because solid fraction drastically increases during slag-gas reaction and heat is generated more than that required for compensation of slag temperature decrease. However, the drastic increase in the amount of produced H_2 gas due to drastic increase of slag temperature is not observed.

Table 1 Conditions for calculation by FactSage 6.2.[6]

Slag preparation	
Reaction	FeO(s) + CaO(s) + SiO_2 (s) → FeO–CaO–SiO_2 (slag) + other condensed phases
Amount	Total: 1 kg
Number of compounds	Total: 56 (Liquid: 7, Solid: 49)
Number of solutions	12 (Species: 39) FACT-SLAG (Slag-liquid), FACT-SPIN (Spinel), FACT-oPry (Orthopyroxene), FACT-cPry (Clinopyroxene), FACT-pPry (Protopyroxene), FACT-WOLL (Wollastonite), FACT-Oli1 (Olivine1), FACT-MeO (Monoxide), FACT-"C2S (a'Ca2SiO4), FACT-Oli2 (Olivine2), FACT-Mel (Melilite), FACT-FeLQ (Fe-liq)
Temperature	Fixed (1873 – 1973 K)
Composition	FeO: 10 – 40 mass%, mass%CaO/mass%SiO_2: 2 or 3
Slag – gas equilibrium	
Reaction	FeO–CaO–SiO_2 (slag) + other condensed phases + H_2O–Ar (g) → FeO–Fe_2O_3–CaO–SiO_2 (slag) + other condensed phases + H_2O–H_2–Ar (g)
Amount	All remaining condensed phases + 10 L of gas (1 calculation)
Number of compounds	Total: 105 (Gas(ideal): 26, Liquid: 9, Solid: 70)
Number of solutions	12 (Species: 40) FACT-SLAGA (ASlag-liquid), FACT-SPIN (Spinel), FACT-oPry (Orthopyroxene), FACT-cPry (Clinopyroxene), FACT-pPry (Protopyroxene), FACT-WOLL (Wollastonite), FACT-Oli1 (Olivine1), FACT-MeO (Monoxide), FACT-"C2S (a'Ca2SiO4), FACT-Oli2 (Olivine2), FACT-Mel (Melilite), FACT-FeLQ (Fe-liq)
Gas temperature	473 – 1273 K
Gas composition	$P(H_2O)$: 0.1 – 1.0 atm
Temperature	Change to satisfy no enthalpy change

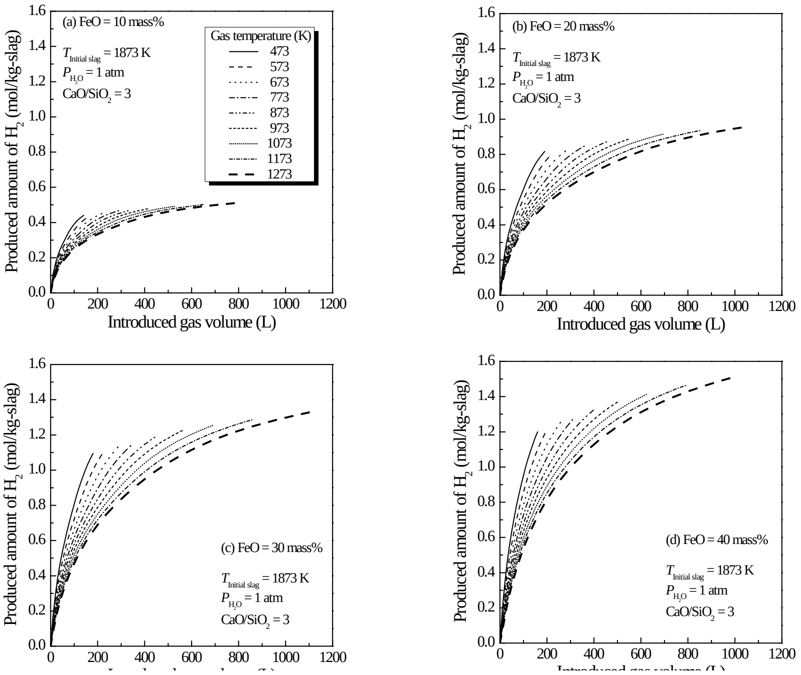

Figure 1 Change in produced amount of H_2 gas with introduced gas volume; initial slag temperature = 1873 K, mass%CaO/mass%SiO_2 ratio = 3, $P(H_2O)$ = 1 atm, initial FeO content: (a) 10 mass%, (b) 20 mass%, (c) 30 mass%, and (d) 40 mass%.[6]

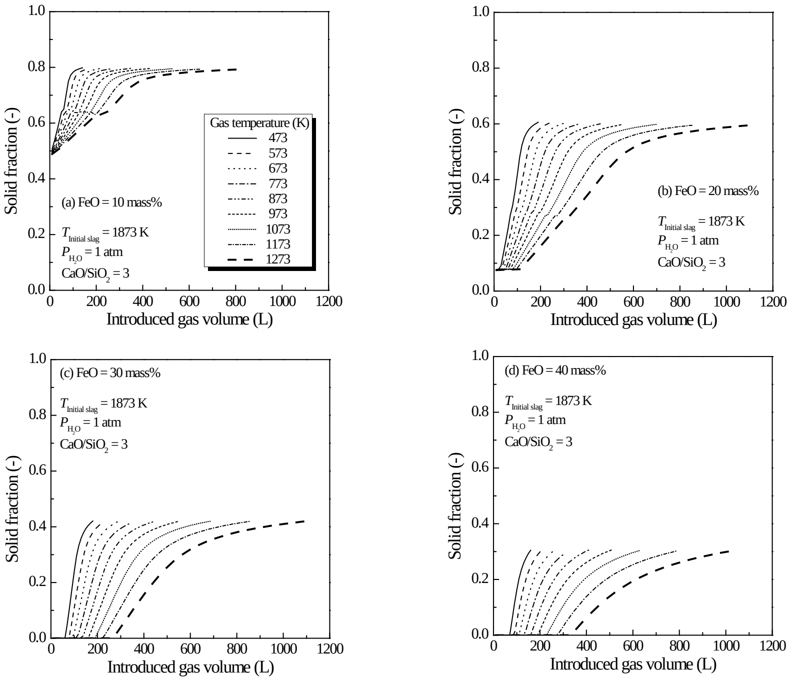

Figure 2 Change in fraction of solid phase in slag with introduced gas volume; initial slag temperature = 1873 K, mass%CaO/mass%SiO_2 ratio = 3, $P(H_2O)$ = 1 atm, initial FeO content: (a) 10 mass%, (b) 20 mass%, (c) 30 mass%, and (d) 40 mass%.[6]

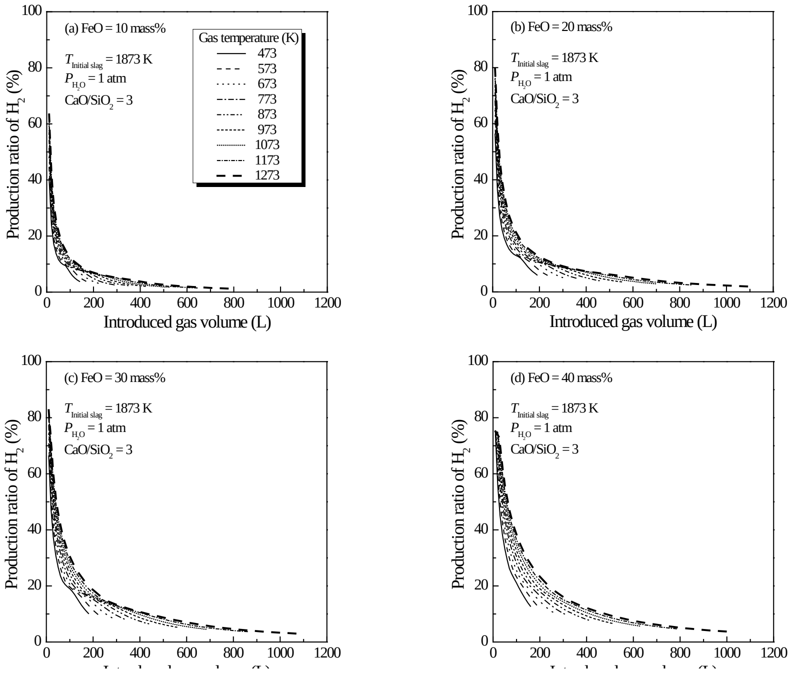

Figure 3 Change in production ratio of H_2 gas with introduced gas volume; initial slag temperature = 1873 K, mass%CaO/mass%SiO_2 ratio = 3, $P(H_2O)$ = 1 atm, initial FeO content: (a) 10 mass%, (b) 20 mass%, (c) 30 mass%, and (d) 40 mass%.[6]

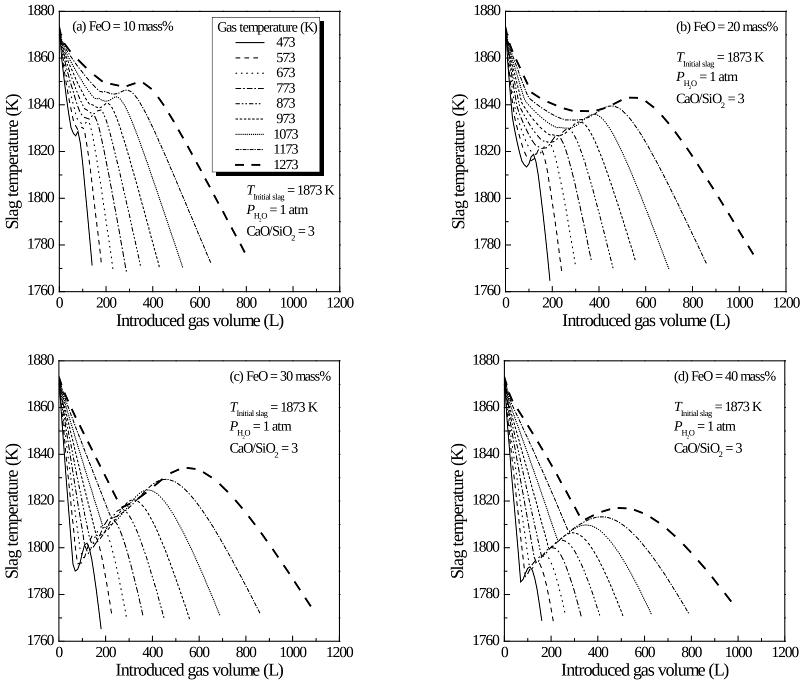

Figure 4 Change in slag temperature with introduced gas volume; initial slag temperature = 1873 K, mass%CaO/mass%SiO_2 ratio = 3, $P(H_2O)$ = 1 atm, initial FeO content: (a) 10 mass%, (b) 20 mass%, (c) 30 mass%, and (d) 40 mass%.[6]

3. Reaction Behavior Between Molten $CaO–FeO–SiO_2$ Slag and $Ar–H_2O$ Gas[7]

3.1 Experimental

The weight change of the $FeO–CaO–SiO_2–Al_2O_3–MgO–P_2O_5$ slag was measured after reaction with gas to measure generation behavior of H_2 gas by reaction between FeO-containing slag and H_2O-containing gas. Slag samples were prepared by following procedures. FeO was prepared by melting equimolar mixture of reagent grade Fe powder and Fe_2O_3 or Fe_3O_4 powder in an iron crucible at 1723 K for 1 h at Ar atmosphere and quenching the melt on a steel plate with blown Ar gas. CaO was prepared by calcining reagent grade $CaCO_3$ in a mullite Tammann crucible at 1273 K for 12 h. Prepared FeO and CaO, and reagent grade SiO_2, Al_2O_3, MgO and $Ca_3(PO_4)_2$ were mixed with prescribed ratios and the mixture was melted in an iron crucible at 1723 K for 1 h at Ar atmosphere. The premelted slag was quenched on a steel plate with blown Ar gas.

Figure 5 shows the schematic diagram of the experimental apparatus, which consists of a gas circuit for preparation of H_2O–Ar gas with constant H_2O partial pressure and an electric furnace with a mullite reaction tube (O.D. 50mm, I.D. 42 mm, length 1000 mm). Three Erlenmeyer flasks with distilled water were connected in series and put inside a thermostat bath kept at 333 K. Argon gas was continuously supplied into flasks with flow rate of 300 cm^3/min and 0.2 atm H_2O–Ar gas was obtained. Further Ar gas was mixed with flow rate of 500 cm^3/min to increase the gas flow rate and finally 0.086 atm H_2O–Ar gas was blown to the surface of molten slags through a mullite tube (O.D. 6 mm, I.D. 4 mm) which tip was kept at the position of 25 mm above the slag surface. A Pt crucible (upper diameter 36 mm, bottom diameter 22 mm, height 40 mm, volume 30 cm^3) was employed to keep 10 g of molten slag at Ar atmosphere. After the slag sample was melted completely, H_2O–Ar gas was introduced onto the sample. Count of reaction time started when the gas was switched. After prescribed reaction time passed, H_2O–Ar gas was changed to Ar gas and the reaction tube was purged, and then the Pt crucible was quickly taken out of the reaction tube and quenched by blowing Ar gas.

Weights of samples with the Pt crucible before and after each experiment were measured, and chemical compositions of slags before and after experimens were analyzed by following methods, total Fe and Fe^{2+} contents by titration method with potassium dichromate, SiO_2 by gravimetry, Al and Mg by ICP-OES of acid solution, and P by molybdenum blue spectrophotometric method.

3.2 Results and Discussion

In the present experiments, 0.086 atm H_2O–Ar gas with flow rate of 875 cm^3/min and 10 g of molten slag was reacted for 15 to 120 min at 1723 K. Four kinds of slags were prepared with various FeO contents and mass%CaO/mass%SiO_2 ratios, while Al_2O_3, MgO and P_2O_5 contents were almost maintained constant, hereafter shown as slags A (FeO = 47 mass%, CaO/SiO_2 = 0.81), B (FeO = 48 mass%, CaO/SiO_2 = 1.28), C (FeO = 36 mass%, CaO/SiO_2 = 0.92) and D (FeO = 28 mass%, CaO/SiO_2 = 0.81), respectively.

Figure 6 shows the relationship between weight increase and reaction time for four slag samples. Weights of all slags increased monotonously with time. The increment at the initial 15 min was the largest and similar for all slags. On the contrary, the increasing rates of slag weights after 15 min were different between slags, which is due to the difference in

FeO content of slags. When all FeO in slags are oxidized to Fe_2O_3, the estimated increase in slag weights are 0.520, 0.538, 0.406 and 0.312 g for slag A, B, C and D, respectively, and the reaction ratios calculated from weight increase are 43.0, 50.5, 32.2 and 32.2 % for slag A, B, C and D, respectively. The reaction ratio increased with increasing initial FeO content in slag. This difference would be due to change of conditions of molten slag surface, such as partial solidification of slag surface because of the oxidation of FeO to Fe_2O_3.

FeO and Fe_2O_3 contents decreased and increased respectively while contents of other oxides did not change clearly, which means FeO was oxidized to Fe_2O_3. Figure 7 shows the change in FeO content of slags with reaction time. FeO contents of all slags decreased monotonously with time. Comparing slags A and B, FeO content of slag B decreased more than that of slag A. Initial FeO contents of these slags were almost the same, however mass ratio of CaO to SiO_2 for slag B was larger than that for slag A. Activity of FeO in slags estimated for the FeO–CaO–SiO_2 system[8] at 1723 K are 0.56 and 0.63 for slags A and B, respectively. Considering reaction (1), larger FeO activity increases the forward reaction rate more. Therefore, FeO in slag B is oxidized more than that in slag A.

In the present experiments, inlet and outlet gases were analyzed by a quadrupole mass spectrometer and significant increase in ion current corresponding to H_2 gas of outlet gas compared to inlet gas was observed, indicating the production of H_2 gas by reaction between FeO-containing slag and H_2O-containing gas.

Present experiments were conducted for slags with mass ratio of CaO to SiO_2 from 0.8 to 1.3 and temperature at 1723 K because of the regulation of experimental setup. Therefore, the direct estimation regarding H_2 gas generation behavior from converter steelmaking slag is difficult. However, for example, in the case of slag D which initial FeO content was 28 mass%, 0.59 mol-H_2/kg-slag were generated after reaction with 0.086 atm H_2O–Ar gas for 120 min. Assuming amount of converter slag generated after one time operation with 300 t capacity converter is 30 t and the same efficiency for H_2 production by slag–gas reaction, 17700 mol or 396 Nm^3 H_2 gas would be produced from this slag. Considering that practical converter slag contains fine steel particles, the amount of produced H_2 gas is expected to increase further. However, when we develop the environmental-friendly H_2 production process with converter slag and H_2O gas, process conditions such as temperature drop, reaction rate between slag and gas or generation of various solid phases from slag with progress of oxidation reaction must be deeply considered.

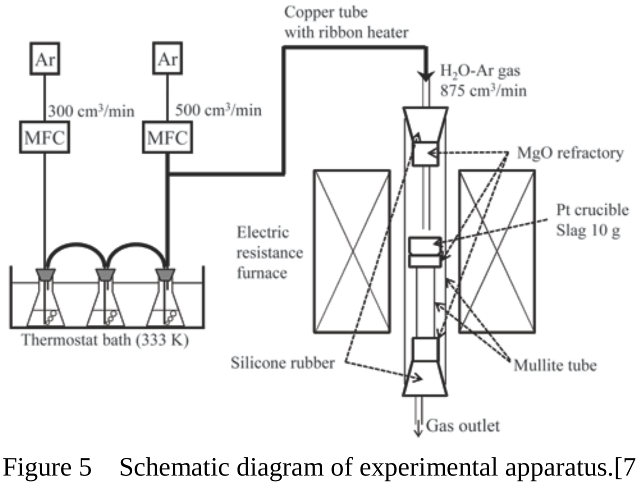

Figure 5 Schematic diagram of experimental apparatus.[7]

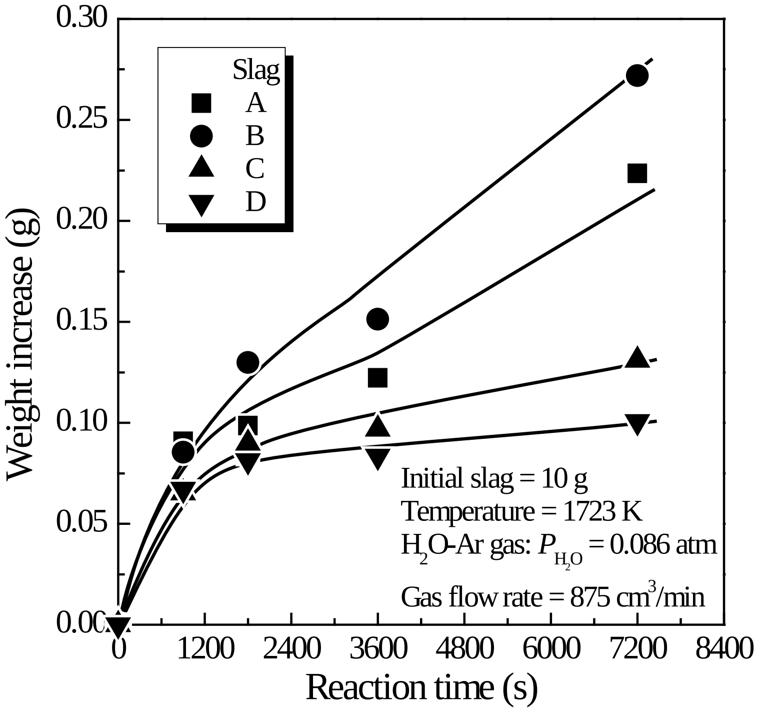

Figure 6 Relationship between weight increase and reaction time.[7]

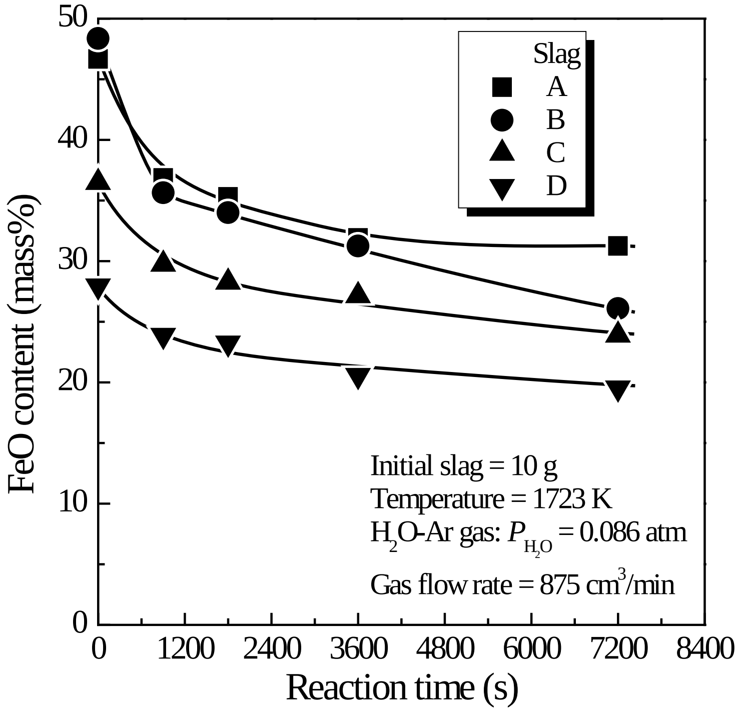

Figure 7 Change in FeO content of slags with reaction time.[7]

4. Conclusions

In the present paper, the recent researches about development of H2 production process with converter slag were reviewed, in which firstly thermodynamic simulations of reaction between steelmaking slag and H_2O–Ar gas were conducted. Increase in initial FeO content increased the amount of generated H_2 gas and increase in gas temperature was effective to produce more H_2 gas by minify temperature drop. Solid fraction would become an important property to be controlled.

Secondly, measurement of generation behavior of H_2 gas by reaction between FeO-containing slag and H_2O–Ar gas was done at 1723 K with four kinds of synthesized FeO–CaO–SiO_2–Al_2O_3–MgO–P_2O_5 slag. From 32.2 to 50.5 % of FeO contained in slags initially were oxidized to Fe_2O_3 by 0.086 atm H_2O–Ar gas for 120 min. Maximal amount of generated H_2 gas estimated from composition change was 0.59 mol-H_2/kg-slag for 120 min at present experimental conditions.

References

[1] Greenhouse Gas Inventory Office of Japan, Center for Global Environmental Research, National Institute for Environmental Studies ed. National Greenhouse Gas Inventory Report of JAPAN, 2011, p2-5, in Japanese.

[2] Nippon Slag Association. Statistics on Iron and Steel Slag (FY2010), 2011, p6, in Japanese.

[3] Kazumi Ogino, Atsushi Nishiwaki, Yasuhiro Habara and Toshihisa Nishino. Measurement of Heat Content of Slag. *Tetsu-to-Hagané*, 1979, 65, S179, in Japanese.

[4] Agency for Natural Resources and Energy, Ministry of Economy, Trade and Industry of Japan. 2010 Annual Report on Energy (Japan’s “Energy White Paper 2010”), 2011, p85, in Japanese.

[5] E. T. Turkdogan. Physical Chemistry of High Temperature Technology, Academic Press, New York, 1980, p11-12.

[6] H. Matsuura and F. Tsukihashi. Thermodynamic Calculation of Generation of H_2 Gas by Reaction Between FeO in Steelmaking Slag and Water Vapor. *ISIJ International*, 2012, 52 (8), in press.

[7] M. Sato, H. Matsuura and F. Tsukihashi. Generation Behavior of H_2 Gas by Reaction Between FeO-Containing Slag and H_2O–Ar Gas. *ISIJ International*, 2012, 52 (8), in press.

[8] Verein Deutscher Eisenhüttenleute ed. SLAG ATLAS 2nd Edition, Verlag Stahleisen GmbH, D-Düsseldorf, 1995, p243.