THERMODYNAMIC ANALYSIS OF HYDROGEN PICK-UP IN STEEL THROUGH MOIST SLAGS[1]

MaríliaGirardi Zorzato[2]
Bayard Beling Morales[3]
Wagner Viana Bielefeldt[4]
Antônio Cezar Faria Vilela[5]

Abstract

During secondary steelmaking, one of the main processes is the reduction of hydrogen levels. However the degassing process and the final predictions of hydrogen levels in steel must presume the existence of a hydrogen pick-up factor in liquid steel, originated from different sources. This work aims to study thermodynamically one of the main contributors to the high final levels of hydrogen in steel: the air humidity captured by the slag and transferred to the liquid steel. To achieve this, the thermodynamic software FactSage is used. The influence of the binary MgO-SiO_2 and ternary CaO-MgO-SiO_2 slag systems to hydrogen pick-up in steel is studied, after exposition of these slags to humidity.

Key words: Thermodynamic simulation; Hydrogen; Moisture; Slag; Secondary Steelmaking.

ANÁLISE TERMODINÂMICA DA INCORPORAÇÃO DO HIDROGÊNIO NO AÇO LÍQUIDO A PARTIR DA UMIDADE NA ESCÓRIA

Resumo

Durante a fabricação do aço, a etapa de refino secundário tem como um de seus objetivos a redução do teor de hidrogênio. Porém, o processo de desgaseificação e as previsões finais do teor de hidrogênio no produto devem presumir a existência de um fator de captura deste gás pelo aço líquido, proveniente de diferentes fontes. Este trabalho tem como objetivo desenvolver um estudo termodinâmico sobre a influência de um dos principais contribuintes com o aumento dos teores finais de hidrogênio: a umidade do ar capturada pela escória e repassada ao aço líquido. Para tanto, é utilizado o programa de simulação termodinâmica FactSage. A influência de sistemas de escórias binária MgO-SiO_2 e ternária CaO-MgO-SiO_2 para o *pick-up* de hidrogênio no aço é estudada, após estes sistemas terem sido expostos à umidade.

Palavras-chave: Simulação termodinâmica; Hidrogênio; Umidade; Escória; Refino secundário.

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[1] *Technical contribution to 67th ABM International Congress, July, 31th to August 3rd,2012, Rio de Janeiro, RJ, Brazil.*

[2] *Physicist, Master Student in Metallurgical Engineering, PPGEM, UFRGS, Brazil.*

[3] *Physicist, Master in Metallurgical Engineering,STE, PPGEM, UFRGS, Brazil.*

[4] *Metallurgical Engineer, Dr.Eng. Professor at DEMET, PPGEM, UFRGS, Brazil.*

[5] *Metallurgical Engineer, Dr.-Ing, Professor atDEMET, PPGEM, UFRGS, Coordinatorof LASID, Brazil.*

1 INTRODUCTION

In steelmaking industry, one of the issues that increases costs and lowers steel quality is the level of hydrogen in steel. The presence of this element is always considered harmful to steel, and is a common cause of defects. When present in high levels, it can even result in hydrogen-induced sticker breakouts in continuous casting.(1)

In solid steel, when hydrogen levels are higher than its solubility level, hydrogen diffuses through the lattice and migrates to areas of stress, e. g. around inclusions. It can lead to problems such as cracks and embrittlement.(2)

To prevent these defects and lower the level of hydrogen in steel, a commonly used process is the degassing in secondary steelmaking.(3) However, this stage occasionally is not enough to meet the product requirements, and an additional stage of annealing, or sometimes even the disposal of steel, becomes necessary.

For the reasons stated above, a suitable option to reduce the time and expenses of steelmaking process is to decrease molten steel hydrogen pick-up, identifying and controlling its sources. Some known sources of hydrogen during secondary steelmaking are steel scrap, slag formers, ferroalloys, and carburizers.(4) Air humidity was also observed to have important influence in steel hydrogen pick-up during secondary steelmaking.(5)

This work aims to quantify the influence of slag to the pick-up of hydrogen during secondary steelmaking, employing the thermodynamics software FactSage. Binary MgO-SiO_2 and ternary CaO-MgO-SiO_2 slag systems will be analyzed.

2 STEEL HYDROGEN PICK-UP THROUGH SLAG

When in direct contact with liquid steel, the water vapor found in air can be transferred to the melt. However, if slag is present between steel and air, the water vapor can dissolve in liquid slag as hydroxyl ion or hydroxyl radical, depending on the slag basicity.(6,7)Once in the slag, hydrogen can be transferred to the steel. After vacuum degassing, the hydrogen levels in the slag are much higher than the predicted metal-slag-gas equilibrium, so that the slag continues to be a hydrogen source to the molten metal even after vacuum treatment.(8) A possible explanation to this phenomenon is that dehydrogenation kinetics of steel is fast in comparison with slag dehydrogenation kinetics.(6)

Different authors have empirically measured the dissolution of water vapor in slag systems.(6,8-10) These measurements normally expose the slag to an atmosphere with constant water vapor partial pressure and temperature, until the saturation solubility has been attained. These authors agreed that the water solubility depends directly on the square root of the water vapor partial pressure. Most of authors also agree that within a range from 1,400°C to 1,600°C, temperature does not have considerable influence in the water content of slags.(11)

As an alternative to experimental measurement, it is possible to predict the water solubility in slags(12) with the use of thermodynamic models. The commercial software FactSage has databases that can be applied to perform simulations of slag/liquid steel/gas equilibria.(7,13)

3 METHODOLOGY

Thermodynamic studies were performed with the commercial software FactSage 6.2. The following databases were used, described according to the FactSage Database Documentation:(14)

- FACT-SLAG - FACT database for liquid oxides. For calculations, the considered components were: CaO, SiO_2, MgO, H_2O, $Ca(OH)_2$, $Mg(OH)_2$.
- FACT-FeLQ - FACT database for liquid Fe with dilute solutes. The considered components for calculations were: Fe, Ca, H, O, Si, Mg, MgO, SiO, CaO.
- FToxid - The FACT database was extensively expanded and optimized for FactSage 5.3, released in 2005. It was divided into FToxid, FTsalt, FThall, FTmisc and Fthelg databases. Among several sub-systems of solutions in FToxid, FToxid-SLAGE was used for the oxide solutions. For calculations, the following compounds were taken into consideration: MgO, FeO, SiO_2, CaO, Fe_2O_3, H_2O, $Ca(OH)_2$, $Mg(OH)_2$, $Fe(OH)_2$.

The software cited above allows one to compute equilibrium state of a thermodynamic system: its components are put in contact under constant pressure and temperature and the computation proceeds until equilibrium is attained. The kinetic of the system is not taken into account in this methodology.

3.1 Simulations

The following simulations were performed:

3.1.1 Simulation 1: Choice of database for calculations of water solubility in slags

A comparison between experimental data obtained by Sosinsky(9) and the numerical results using FactSage was done. For this comparison, two different databases were selected: i) the former FACT-SLAG database; and ii) the FToxid-SLAGE database.

This simulation reproduced the same conditions used by Sosinsky: slag compositions, temperatures and water vapor partial pressures. Basically, the slags were exposed to an argon/water vapor mixed atmosphere, until equilibrium was reached. Temperature and water vapor partial pressure were held constant during each simulation experiment.

The water solubility of four different slag compositions (Table 1) was observed for different values of temperature (from 1,375ºC to 1,575ºC) and water vapor partial pressure (approximately from 0.037 atm to 0.114 atm).

Table 1. Slag compositions used in Simulation 1(9)

	Slag composition (WtPct)		
Slag	CaO	MgO	SiO_2
Slag1	13.1	30.0	56.9
Slag2	25.6	17.2	57.2
Slag3	30.0	20.0	50.0
Slag4	0	38.8	61.2

The results of Simulation 1 are moist slag compositions in equilibrium with an atmosphere formed by argon and water vapor at constant partial pressures, with the total pressure of the system being equal to 1 atm.

Another important point is that the components of the initial slags used in Simulation 1 are moisture-free, as seen in Table 1. It means that the presence of moisture contained in the slag formers is not considered.

3.1.2 Simulation 2: Contribution of Sosinsky's moist slags to hydrogen content in Fe

The moist slag compositions obtained from Simulation 1 were used as initial data with some amount of pure iron, where:

- Slag/iron weight proportion was 1:10.
- Temperatures from Simulation 1 were kept the same.
- Atmosphere humidity was not taken into account.
- FToxid-SLAGE and FACT-FeLQ databases were used.
- The total pressure of the system was equal to 1 atm.

This simulation aimed to estimate the amount of hydrogen that is transferred from moist slag to iron. So, Simulation 2 only takes into account the water already present in the slag, and the results of this simulation show the amount of hydrogen in the iron that is in equilibrium with the final amount of hydrogen in the moist slag.

3.1.3 Simulation 3: Contribution of different slag compositions to hydrogen content in Fe

Different CaO-MgO-SiO_2 slag compositions (Table 3) were studied in order to estimate the water solubility in these slags and their contribution to hydrogen pick-up in Fe at 1,600ºC. This simulation occurred in two steps, which are basically equivalent to Simulation 1 and 2:

a) The slag was exposed to an atmosphere composed of argon and water vapor at partial pressure until equilibrium was reached, where:

- Temperature was fixed in 1,600ºC.
- The water vapor partial pressures used were chosen to be consistent with the water vapor partial pressures encountered in air at temperatures between 15 and 40ºC, when the relative humidity is 100%. For these calculations, the following formula was used:(15)

  $$p_S = 610.78 \cdot \exp\left(\frac{T \cdot 17.2694}{T + 238.3}\right)$$

  Where p_S is the water saturation vapor pressure in Pascal, and T is the temperature in degrees Celsius. When the relative humidity of air is 100%, the saturation vapor pressure equals the water partial pressure. For temperatures between 15ºC and 40ºC the values for water vapor partial pressures were between 0.0167atm and 0.0721atm.
- Slag compositions are listed in Table 3.
- FToxid-SLAGE database was used.
- The total pressure of the system was equal to 1 atm.

b) Each moist slag resulting from (a) was the initial data in this step, with some amount of Fe, where:

- Temperature was fixed in 1,600ºC.
- Slag-Fe weight proportion was 1:10.
- Atmosphere humidity not considered.
- FToxid-SLAGE and FACT-FeLQ databases were used.
- The total pressure of the system was equal to 1atm.

The results of Simulation 3a are moist slag compositions in equilibrium with an atmosphere formed by argon and water vapor at constant partial pressures. As in Simulation 1, the components of the initial slags used in Simulation 3a are moisture-free.
The results of Simulation 3b show the amount of hydrogen that is transferred from the moist slag to the iron. This amount of hydrogen in the iron is in equilibrium with a final amount of hydrogen in the moist slag.

4 RESULTS AND DISCUSSION

FactSage calculates the thermodynamic equilibrium for the systems, without considering reaction kinetics. It means that the equilibrium values are the highest possible for the temperatures and pressures considered. So, hydrogen contents obtained with the simulations are expected to be equal to or higher than those empirically measured.

4.1 Results of Simulation 1

Figures 1a to 1d show the difference between the results obtained by Sosinsky and the results obtained with FToxid-SLAGE and FACT-SLAG databases in Simulation 1.The FToxid-SLAGE database results were more similar to Sosinsky's results.In this way,this database was chosen to be used in Simulations 2 and 3.
The relationship between hydrogen content in the slag and the square root of the water vapor partial pressure is linear, even with a temperature range from 1,375°C to 1,575°C. This relationship was found in Sosinsky's experiments and in the simulations presented in this work. The results of Simulation 1 also show that the FactSage databases can be applied to estimate the water content in slags due to air humidity.

Figure 1a Figure 1b

Figure 1c Figure 1d

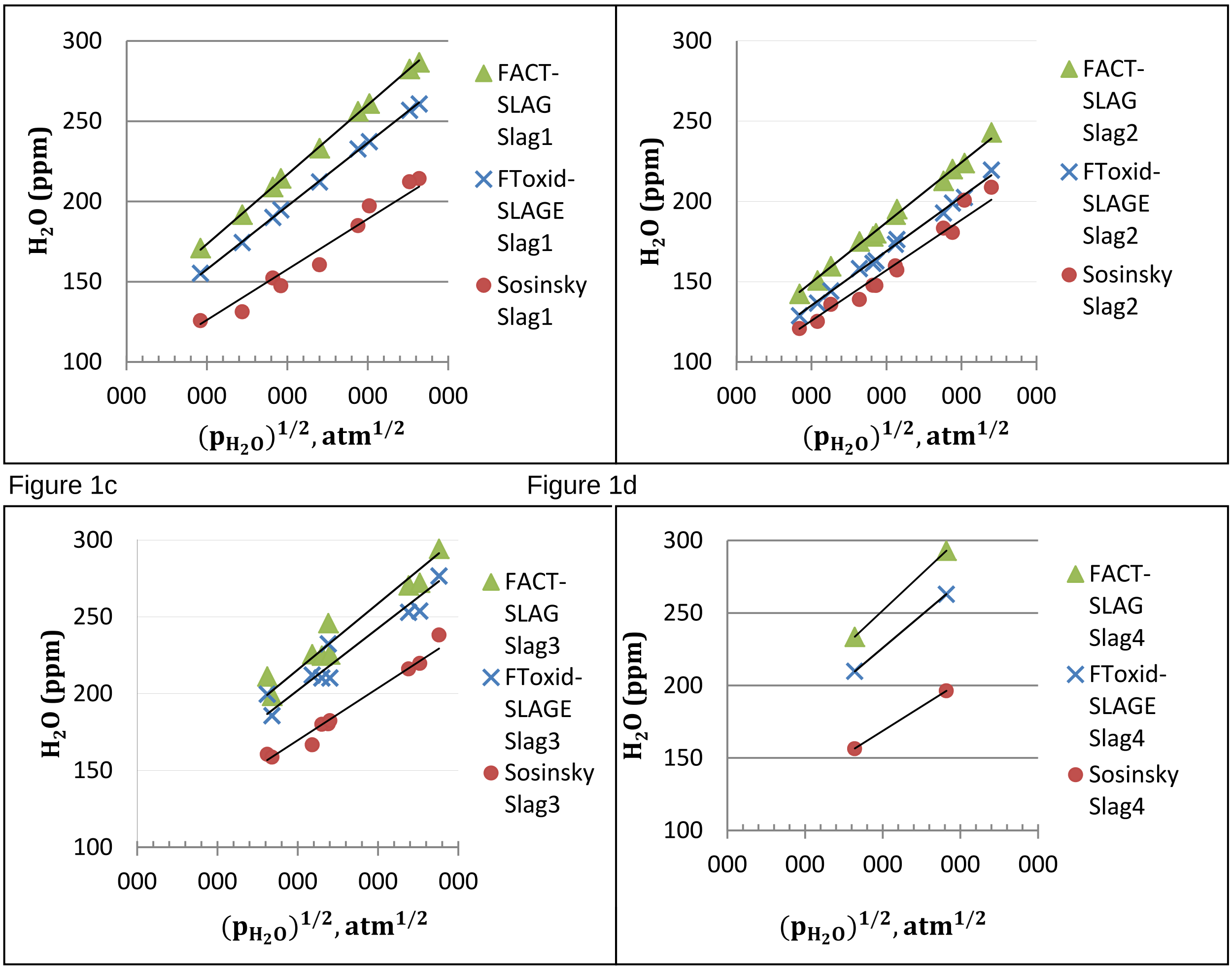

Figure 1. Comparison between Sosinsky's empirical measures and results obtained with FToxid-SLAGE and FACT-SLAG FactSage databases. Water solubilities in slags *versus* water vapor partial pressures are plotted. a) Water solubility in Slag1; b) Water solubility in Slag2; c) Water solubility in Slag3; d) Water solubility in Slag4.

Table 2 is a compact presentation of the input and output data intervals from Simulation 1 using FToxid-SLAGE. The hydrogen content in the slag was calculated and is also shown in Table 2.

Slag4 is the slag that more absorbs water, while Slag2 is the one that absorbs less.

Table 2. Input and output data intervals from Simulation 1 using FToxid-SLAGE

Input			Output	
Slag	Temperature (ºC)	H_2O partial pressure in contact with slag (atm)	Water solubility in slag (ppm H_2O)	Hydrogen content in slag (ppm)
Slag1	1,525 – 1,575	0.038 - 0.110	155.2 - 260.7	17 - 29
Slag2	1,400 – 1,575	0.037 - 0.102	128.8 - 219.5	14 - 24
Slag3	1,375 – 1,575	0.053 - 0.114	199.7 - 253.8	20 - 31
Slag4	1,575	0.054 - 0.085	209.8 - 263.0	23 - 29

4.2 Results of Simulation 2

Figure2 shows the final hydrogen contents in Fe,obtained in Simulation 2. As stated before, the initial slag composition in this simulation is the moist slag obtained as output of Simulation 1. The observed amount of hydrogen that was transferred from themoist slags to iron melt was between 9.4% and9.6% of the total initial hydrogen content in the slag. This means that the Fe melt may pick-up from 1 ppm to 3 ppm of hydrogendue to slag moisture.

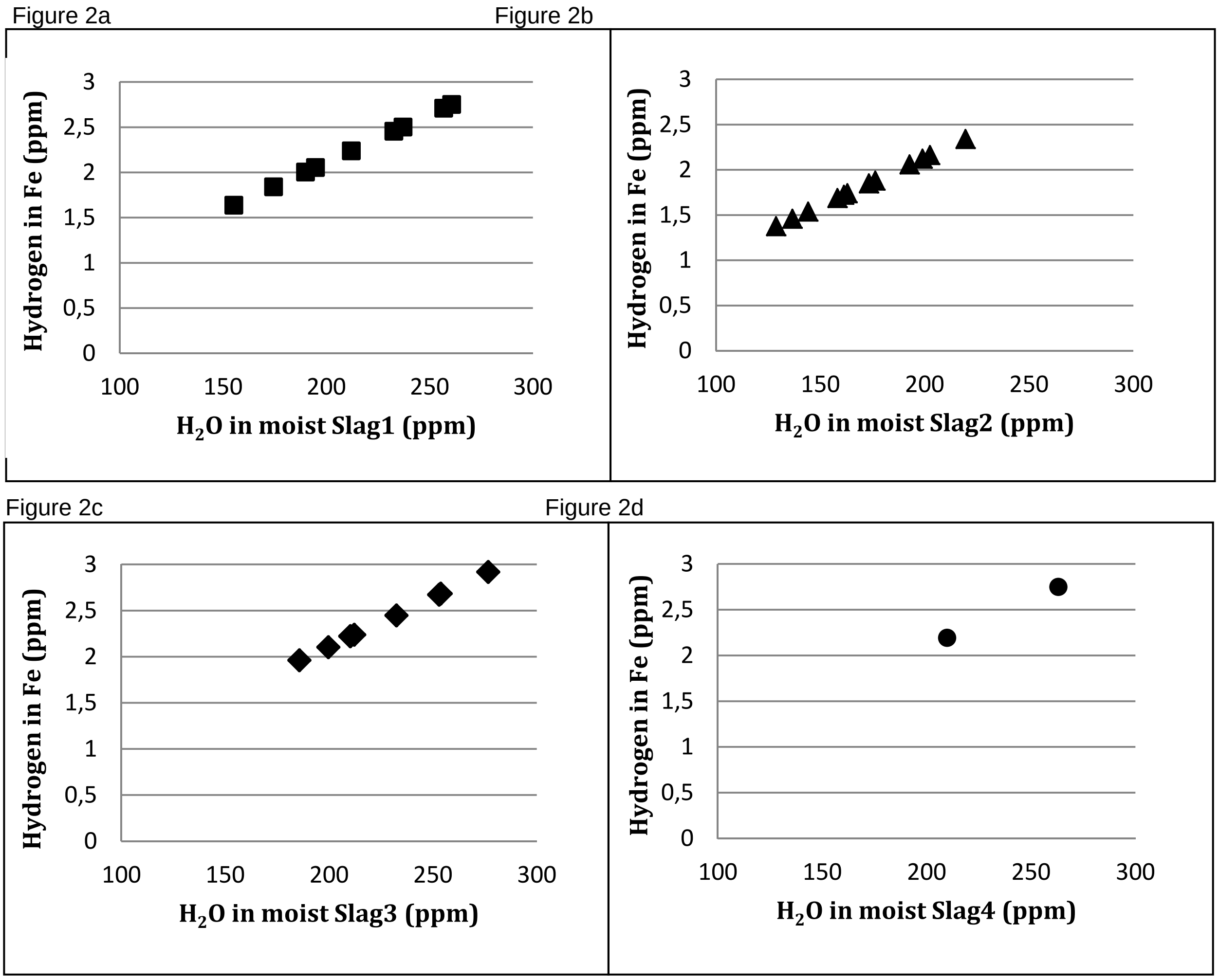

Figure 2. Plots of final hydrogen content in Fe as a function of the initial water content in moist slags.a) Steel hydrogen pickup from moist Slag1; b) Steel hydrogen pickup from moist Slag2; c) Steel hydrogen pickup from moist Slag3; d) Steel hydrogen pickup from moist Slag4.

4.3 Results of Simulation 3

Slag compositions and results from Step (a) and Step (b) are in Table 3.
Slags with high CaO contents can contribute more to the hydrogen pick-up in iron. MgOalso contributesto increase themoistureof the slag,and therefore the content of hydrogenin the liquid steel. These can be seen in Figure 3. Figure 3 shows solubility of H_2O in $CaO-SiO_2-MgO$ melts at 1,550°C and water vapor pressure $P_{H_2O} = 0.385$ bar in (Ar + H_2O) atmosphere.(16) Water solubility increases with CaO and MgO contents in slags.
The hydrogen content in iron has a linear dependence on slag moisture content in the studied interval of water solubility. This dependence shows that in average 8% of the hydrogen content in themoist slags from Table 4 is transferred to iron.

Table 3. Slag compositions used in Simulation 3 and results obtained

	Slag composition (Wt Pct)			Water solubility in slag (ppm H_2O) – Step (a)	Hydrogen content in Fe after contact with humid slag (ppm) – Step (b)
Slag	CaO	MgO	SiO_2		
Slag 1	60	10	30	1,381 – 2,848	12.44 – 24.22
Slag 2	40	40	20	1,566 – 3,244	14.35 – 28.32
Slag 3	35	30	35	632 – 1,306	5.92 – 12.04
Slag 4	30	30	40	232 – 480	2.33 – 4.81
Slag 5	25	50	25	1,073 – 2,223	9.89 – 19.83
Slag 6	20	40	40	291 – 602	2.86 – 5.89
Slag 7	20	60	20	1,236 – 2,562	11.33 – 22.60
Slag 8	10	60	30	708 – 1,469	6.59 – 13.46

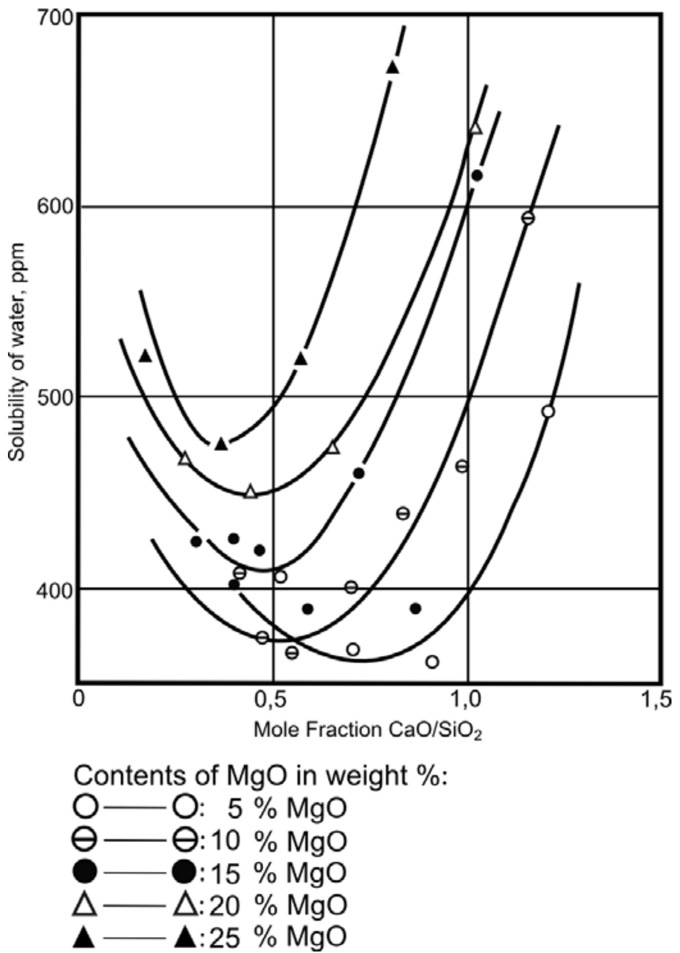

Figure 3. Solubility of H_2O in $CaO\text{-}SiO_2\text{-}MgO$ melts at 1550°C and P_{H2O} = 0.385 bar in (Ar + H_2O) atmosphere.(16)

5 CONCLUSIONS

The thermodynamic software FactSage can be applied for calculations of water solubility in slags, showing good accordance with literature data. As CaO and MgO contents in ternary CaO-MgO-SiO_2 slags increase, water solubility also increases. This phenomenon is attenuated by addition of SiO_2 contents in slags.

When used to quantify the contribution of slag moisture to hydrogen content in Fe, the FactSage estimates show that this contribution is important to be considered in the steelmaking process.The simulations showed that the hydrogen content in Fe depends on slag composition and also on the water vapor partial pressure to which the slag was exposed to.

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REFERENCES

1 MISRA, S.; LI, Y.; SOHN, I. Hydrogen and Nitrogen Control in Steelmaking at U. S. Steel. AISTech, 2009.
2 HURST, C. R.; VERGAUWENS, M. Gas Analysis in Steel: Identifying, Quantifying, and Managing Hydrogen Pick Up in Steel.
3 CELIBERTO, A. M.; Desgaseificação A Vácuo e Práticas Operacionais Para Produção De Aços Especiais Numa Aciaria Elétrica. Graduate thesis, Universidade Federal do Rio Grande do Sul, 2004.
4 HENRIQUES, B. R.; ARAÚJO, F. G. S.; OLIVEIRA, C. P.; Caracterização da Incorporação de Hidrogênio na Aciaria da Arcelormittal Tubarão. 41st Steelmaking Seminar - International, ABM, 2010.
5 FUJII, T.; MANETTA, H. R.; FERREIRA NETO, O. A.;CASTRO, L. F. A.; Estudo da Incorporação e Controle do Hidrogênio na Aciaria da V&M do Brasil. Seminário de Fusão, Refino e Solidificação dos Metais. 33, 2003. ABM.
6 JO, S-K.; Kim, S-H.; The solubility of Water Vapour in $CaO-SiO_2-Al_2O_3-MgO$ Slag System. Steel Research, Vol.71, 2000.
7 JUNG, I-H.; Thermodynamic Modeling Of Gas Solubility In Molten Slags (II) - Water. ISIJ International, Vol. 46, 2006.
8 DOR, B. C.; GATELLIER, N. C.; Influence Du Laitier Sur La Déshydrogénation De L'acier Sous Vide. La Revue de Métallurgie, 1988.
9 SOSINSKY,D.J.; MAEDA, M.;MCLEAN, A.; Determination and Prediction of Water Vapor Solubilities in $CaO-MgO-SiO_2$ Slags. Metall. Trans. B, Vol. 16B, 1985.
10 BRANDBERG, J.; SICHEN, D.; Water Vapor Solubility in Ladle-Refining Slags. Metall. Trans. B, Vol. 37B, 2006.
11 DAYA, Z.; The Thermodynamics Of Water Vapour Dissolution In Tindish Fluxes. Graduate Thesis, University of Toronto, 1997.
12 SOMMERVILLE, I. D.; The Measurement, Prediction and Use of Capacities of Metallurgical Slags. Scaninject IV, 1986.
13 KANG, Y-B.; PELTON, A.; Thermodynamic Model And Database For Gaseous Species In Molten Oxide Slags. Molten 2009.
14 FACT oxide database, www.factsage.com (accessed 2012).
15 http://www.natmus.dk/cons/tp/atmcalc/atmoclc1.htm - Water vapor pressure calculations (accessed 2012).
16 IGUCHI, Y; T. FUWA; Trans. Iron Steel Inst. Japan 10, 1970.