

CO-UTILIZATION OF SLAGS FROM DIFFERENT INDUSTRIAL PROCESSES TO GENERATE FUEL GASES, REDUCE CO₂ EMISSIONS, AND THE POTENTIAL IMPACT OF SLAG CHANGES ON REFRACTORY WEAR

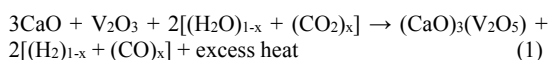
Jinichiro Nakano^{1,2}, Anna Nakano^{1,2}, and James Bennett¹

¹U.S. Department of Energy National Energy Technology Laboratory; Albany, OR, USA

²AECOM; Albany, OR, USA

ABSTRACT

Iron & steelmaking and slagging gasification processes utilize carbon feedstock such as coal and petroleum coke (petcoke) in the production of metal, power, and/or chemicals; but they also generate large quantities of greenhouse gases (high in CO₂) and slag as by-products. The chemistry of slags, whenever possible, is adjusted to maximize refractory service life. Once generated by a process, alternative applications for industrial slags do not always exist. Applications for industrial slags need to be considered in the future, especially those that may reduce greenhouse gases. Typical iron & steelmaking slags are rich in calcium oxide, while petcoke slags from gasification are rich in trivalent vanadium oxide. This study discusses a potential method to simultaneously use gasification and metallurgical slags to generate gaseous fuels (CO and/or H₂) by utilizing the strong chemical affinity of calcium oxide to vanadium oxide under certain conditions. If metallurgical and gasification slags are mixed at a specific ratio in the presence of industrial process waste containing H₂O and CO₂; then the calcium would influence the valence of vanadium in the gasifier slag, changing it from 3+ to 5+, and forming calcium orthovanadate (3CaO·V₂O₅). Note that because of the reducing environment in gasifiers, vanadium in gasifier slag as it exits the gasifier exists in the +3 state. The source of water in the proposed reaction can be waste CO₂ or water, which would be converted to H₂ and/or CO by the reaction. The vanadate formation is expected to occur by removing oxygen from the surrounding introduced gases by the following reaction:



Excess heat generated from the reaction can be used in other processes; such as ore reduction, turbine power generation, and synthetic liquid/gaseous fuel production.

This work discusses thermodynamic computational simulations to explore optimal conditions for the conversions following laboratory results on CO₂ conversions using synthetic mixed slags. It was found that appropriate compositions of the slag mixtures needed to maximize the conversion will alter slag chemistry – potentially impacting refractory service life and/or producing a slag of different viscosity.

INTRODUCTION

Process byproducts such as H₂O, CO₂ and slag from iron & steelmaking and slagging gasification processes used in the production of metal, power, and/or chemicals may be utilized to produce power or useful chemicals. 1.5 tons of CO₂ is emitted per ton of iron produced, and it is estimated an additional 0.9 tons of CO₂ per ton of steel production are generated from subsequent steelmaking processes within the process waste streams [1]. Approximately 523 million tons/year of slag is generated from the iron & steelmaking industry worldwide [2], with less than 65 wt.% of it recycled

or reused [3]. Currently, gasifiers generating 174 gigawatts (thermal) have been or are projected to be built worldwide by 2019 [4], including the Jamnagar Gasification Plant in India, which would generate 9.8 gigawatts (thermal) syngas output utilizing 100% petcoke feedstock [5]. When the existing worldwide gasifier facilities using petcoke as a carbon feedstock are combined with the new plants coming on-line by 2019 [4], a total of 310 gigawatts (thermal) will be produced, generating up to 23,560 tons of petcoke slag every day.

Previous research [6, 7], as shown in Fig.1, empirically demonstrated that by mixing gasification and metallurgical slags at a specific ratio in a CO₂ enriched environment, exothermic heat generated from the reaction would be enough to transform CO₂ to CO. The CO generated could be used to support the existing energy or chemical production, reducing carbon emissions per unit product. In this work, theoretical simulations were performed to guide the determination of optimal conditions to maximize the conversion phenomena. Effects of varying parameters on CO₂ conversion and H₂ production are discussed.

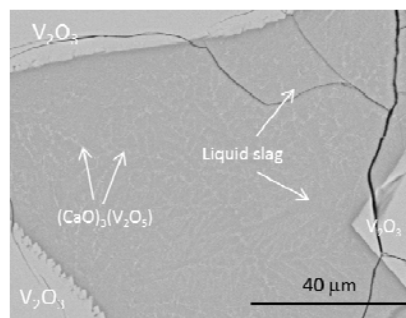


Fig. 1: Scanning electron microscope image of mixed slag from previous research trials studying fuel production by mixing gasifier slag with metallurgical slag.

SIMULATION APPROACH

To understand general trends of the slag mixing conversion reactions influenced by input parameters and conditions, thermodynamic simulations were conducted using FactSage 7.0 with databases of FactPS and FToxid [8]. In the thermodynamic calculations, compositions of metallurgical slag and gasifier slags (petcoke ash) were estimated by averaging values for iron and steelmaking and petroleum coke reported in [6] for simplicity. Only Al₂O₃, CaO, FeO, SiO₂, and V₂O₃ were considered as slag constituents in the simulations. CaO, FeO, and V₂O₃ additions (as additives) to metallurgical slag, gasifier slag, and mixtures thereof were varied from 0 – 30 wt.% at different ratios to determine effects of individual slag constituents. Reaction temperatures were varied from 1000 to 1400 °C. Reactions involving CO₂ and H₂O were assumed to use “pure – 100%” materials in the calculations. Slag mixture:gas ratios equaled 1:1 on a mass basis in the calculations unless indicated otherwise. Note no interaction between slag and vanadium oxide were assumed due to a lack of such data in

the current FactSage databases and based on laboratory studies. Equilibrium calculations with calcium vanadate above 1380 °C were extrapolated using data below that temperature. A total of approximately 4,000 points were calculated and graphically summarized.

RESULTS AND DISCUSSION

With the aim of production of CO and H₂ using slag mixtures, theoretical CO₂ and H₂O conversion rates were determined with respect to slag ratios (metallurgical slag to petcoke ash), temperature, and V₂O₃ as shown in Figs. 2 and 3. With no V₂O₃ addition (i.e., external additive), blending petcoke ash with 20 – 30 wt.% metallurgical slag would maximize the conversions as V₂O₃ is already present in the petcoke ash. For both conversions, the higher slag V₂O₃ concentration by the V₂O₃ additive exhibits a greater effect on the metallurgical slag rich side. The V₂O₃ additions have minimal effects on both conversions on the petcoke ash richer side. At 1000 °C (not shown in figures), higher CO₂ conversion may be achieved if 10 wt.% V₂O₃ is added to the 100 wt.% metallurgical slag. Note at 1000 °C, more solid state reaction is assumed other than liquid state reaction at higher temperatures. The most effective addition of V₂O₃ was located around 20 wt.% for 1200 – 1400 °C. The higher H₂O conversion rate can be achieved around 10 – 20 wt.% V₂O₃ additions to the metallurgical slag rich mixtures.

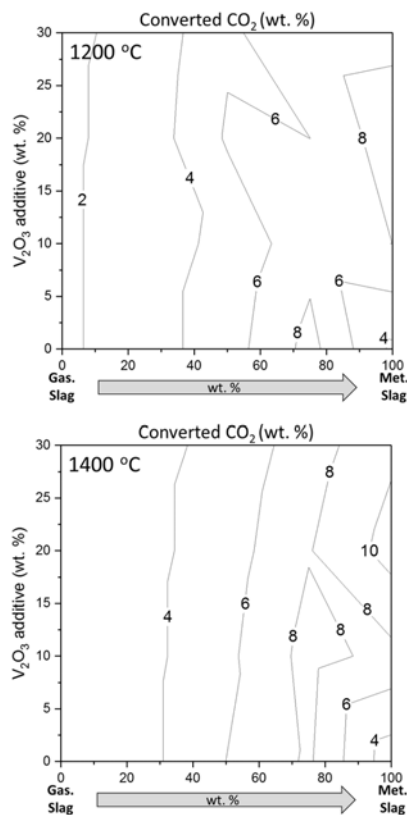


Fig. 2: Effects of additional V₂O₃ in slag on CO₂ conversion.

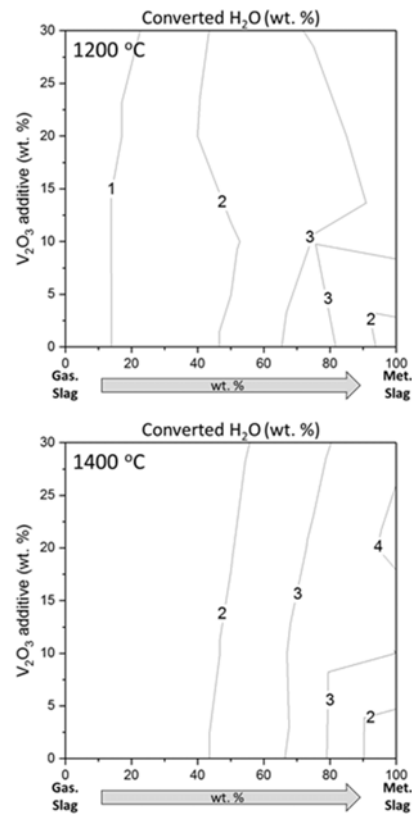


Fig. 3: Effects of additional V₂O₃ in slag on H₂ production.

Figs. 4 and 5 show effects of the CaO addition (as additives) to the averaged slag mixtures at different temperatures. Good conversion rates may be achieved without needing to use V₂O₃ additives if the petcoke ash is added to metallurgical slag at 10 – 30 wt.%, supplying sufficient amounts of V₂O₃. The CaO addition is more effective on the CO₂ and H₂O conversions to the petcoke ash rich side other than the metallurgical slag rich side as more V₂O₃ from the petcoke is available to induce reaction (1). The CaO addition (such as lime) to the petcoke ash may contribute more to the conversion rates when compared to the V₂O₃ addition to the metallurgical slag. Excessive CaO addition seems to have negative effects on the conversions.

The impact of FeO additions (as additives) to the slag mixtures on CO₂ and H₂O conversions are shown in Figs. 6 and 7. The FeO addition exhibited the greatest impact if the petcoke ash is blended to the metallurgical slag in a 25 – 35 wt.% range. The FeO effect, however, was smaller on the petcoke ash richer side and on the metallurgical slag rich side. Iron oxide, if present as FeO, would take oxygen from CO₂ and H₂O by transforming to Fe₃O₄ or Fe₂O₃, enhancing the conversion.

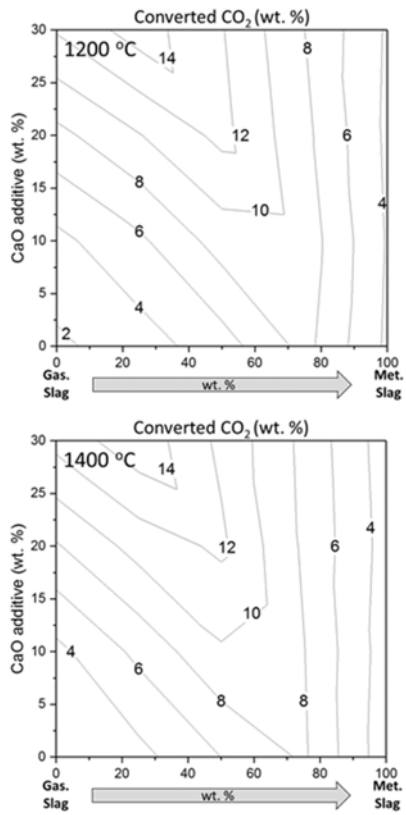


Fig. 4: Effects of additional CaO in slag on CO₂ conversion.

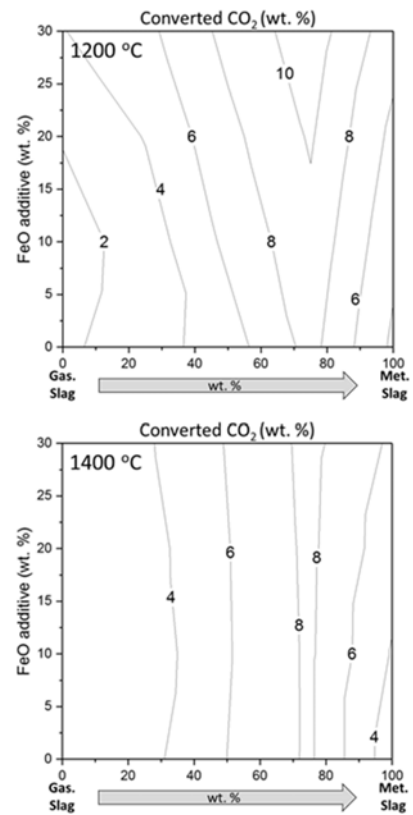


Fig. 6: Effects of additional FeO in slag on CO₂ conversion.

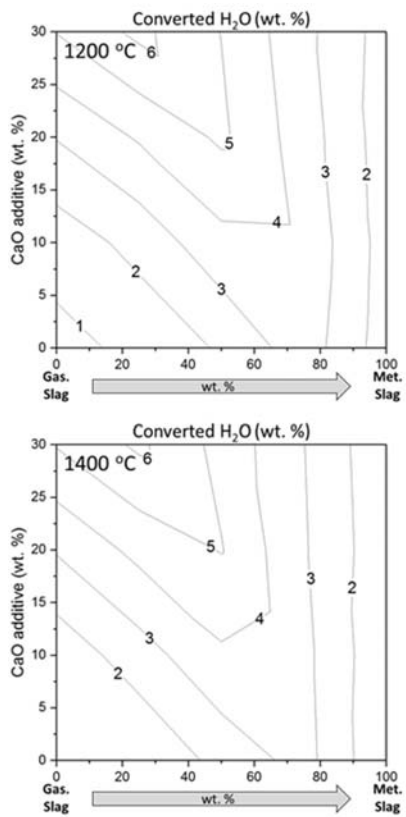


Fig. 5: Effects of additional CaO in slag on H₂ production.

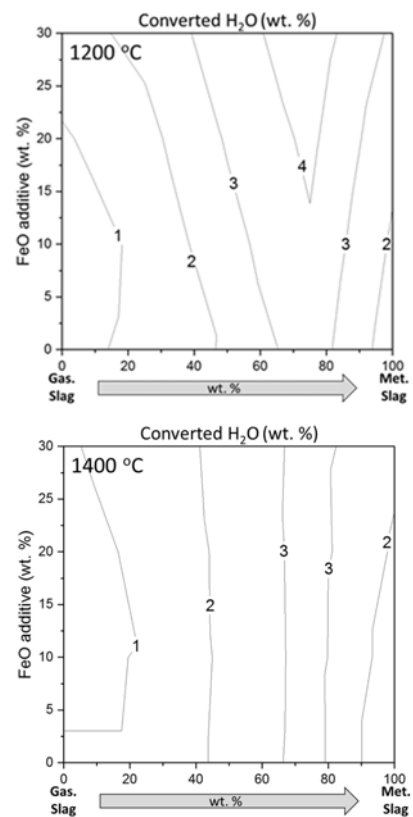


Fig. 7: Effects of additional FeO in slag on H₂ production.

These simulations indicated the presence of thermodynamic realms where the most efficient production of CO and H₂ (i.e., conversions of CO₂ and H₂O) occurred. Slag compositions may be modified before entering a reactor, but may be changed later with additives to optimize the conversion reactions. For the former, the altered compositions must be carefully considered for impacts on refractory service life and gasification and metallurgical efficiency. High levels of some oxides in the slag may result in viscous mix that requires high temperature to flow from the gasifier, accelerating refractory wear and corrosion.

While the laboratory testing and thermodynamic simulations exhibited promising results, it must be noted that the practicality of the conversion process will be limited by the amount of slags available and the chemistry of those slags. If the process is practiced at a 20 kt steel/d metallurgical plant, 195 MW power could be generated using the fuels (CO or H₂) produced from this method while reducing 1 million tons of CO₂ emission. 2 MW would be generated while reducing 7 kilo tons of CO₂ emission if practiced at a 1000 MW gasification site using petcoke feedstock. The limitation of the latter reflects the amount of slag available from the petcoke gasification process (ash content estimated to be approximately 1 wt.% of petcoke). Energy values drastically increases if carbon content (up to 89 wt.% in petcoke slag) and FeO (up to 9 wt.%). Note concentrations of vanadium and calcium, and ash quantity vary with slags.

CONCLUSIONS

The effect of V₂O₃, CaO, and Fe₂O₃ constituents in slag, the reaction temperatures, and the slag ratios CO₂ reduction and H₂ production were discussed using thermodynamic simulations. As shown by the empirical conversion value, a higher conversion may be achieved if a smaller amount of gas input compared to slag, is used. The simulation indicated the possibility of reducing CO₂ emission and/or H₂ production by mixing slags from different industrial sectors. Sources and chemistry of the slags may be appropriately selected to achieve the optimal slag chemistry. The altered slag chemistry, if modified before entering the reactors, would affect the refractory service life and gasification and metallurgical efficiency, changes which if practiced, would require a further study.

ACKNOWLEDGEMENT

This technical effort was performed in support of the National Energy Technology Laboratory's ongoing research under the RES contract DE-FE0004000.

DISCLAIMER

"This project was funded by the Department of Energy, National Energy Technology Laboratory, an agency of the United States Government, through a support contract with AECOM. Neither the United States Government nor any agency thereof, nor any of their employees, nor AECOM, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

REFERENCE

- [1] Fruehan RJ. Research on Sustainable Steelmaking. Metall Mater Trans B. 2009;40:123-33.
- [2] Barati M, Esfahani S, Utigard TA. Energy recovery from high temperature slags. Energy. 2011;36:5440-9.
- [3] Semykina A, Shatokha V, Iwase M, Seetharaman S. Kinetics of Oxidation of Divalent Iron to Trivalent State in Liquid FeO-CaO-SiO₂ Slags. Metall Mater Trans B. 2010;41:1230-9.
- [4] U.S. Department of Energy National Energy Technology Laboratory. Gasifipedia. <http://www.netl.doe.gov/File%20Library/Research/Coal/energy%20systems/gasification/gasifipedia/index.html>.
- [5] Gasification Technology Council. World Gasification Database. <http://www.gasification.org/>.
- [6] Nakano J, Bennett J. CO₂ and H₂O gas conversion into CO and H₂ using highly exothermic reactions induced by mixed industrial slags. Int J Hydrogen Energ. 2014;39:4954-8.
- [7] Nakano J, Bennett J, Nakano A. Energy generation from waste slags: beyond heat recovery. Proceedings for TMS 2016, Nashville, TN, February 14-18, 2016. 2016:131-6.
- [8] Bale CW, Belisle E, Chartrand P, Decterov SA, Eriksson G, Hack K, et al. FactSage thermochemical software and databases - recent developments. Calphad. 2009;33:295-311.

Mailing address

Jinichiro Nakano
U.S. Department of Energy
National Energy Technology Laboratory
1450 Queen Ave. S.W.
Albany, OR, 97321-2198, U.S.A.