

## ENERGY GENERATION FROM WASTE SLAGS: BEYOND HEAT RECOVERY

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### Abstract

In this study, metallurgical and gasification slags mixed at a specific composition were heated to a slag discharge temperature range (*i.e.*, tap out temperatures in iron & steelmaking) in the presence of CO<sub>2</sub>, resulting in a reaction generating energy – enough to convert CO<sub>2</sub> to CO which can be used in other processes such as ore reduction, gas turbine power generation, and synthetic liquid/gaseous fuel production. Computational simulations suggested that the generation of H<sub>2</sub> from H<sub>2</sub>O would also be possible using the same mixed slag approach at no additional heat supply. Energy generated from the reaction remains largely in excess after conversion (CO<sub>2</sub> to CO), which can be utilized independently for or support other processes. Furthermore, a final slag volume is expected to decrease to about 30%, dramatically decreasing landfill burden.

### Introduction

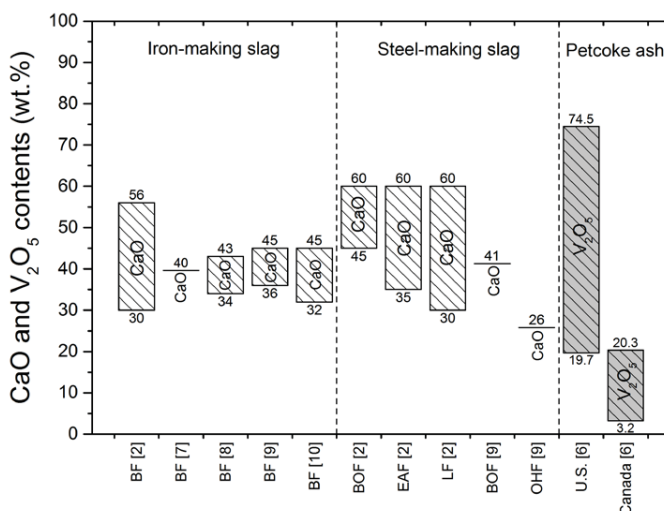
Iron & steelmaking and slagging gasification processes utilize carbon feedstock such as coal and petroleum coke (petcoke) in production of metal, power, and/or chemicals; but also generate large quantities of gas (high in CO<sub>2</sub>) and slag as waste byproducts. In the course of processing, slag forms as molten agglomerates from non-volatile components in feedstock, additives, and/or metal ores' impurities. For every ton of hot metal (iron) production, 1.5 tons of CO<sub>2</sub> is emitted while additional 0.9 tons of CO<sub>2</sub> per ton of steel produced is generated from subsequent steelmaking processes [1]. Reportedly, approximately 523 million tons of slag is annually generated from the iron & steelmaking industry worldwide [2] and less than 65 wt.% is utilized for recovering valuable elements [3]. In the gasification industry, for example, a 500 megawatts (thermal) slagging gasifier used for power/chemical generation operating at a 35% efficiency would need 3,800 tons petcoke carbon feedstock per day, producing approximately 38 tons/day of slag. Currently in the world, gasifiers worth 174 gigawatts (thermal) are being built for 2016 and planned for 2019 [4], including Jamnagar Gasification Plant in India with 9.8 gigawatts (thermal) syngas output [5]. With the existing plants worldwide, gasifiers worth a total of 310 gigawatts (thermal) would be in operation by 2019 [4], generating up to 23,560 tons petcoke slag every day worldwide, depending on the petcoke usage.

Typical iron & steelmaking slags are rich in calcium oxide while petcoke slags from gasification are rich in vanadium oxide as shown in Figure 1 where literature data [2, 6-10] were graphically summarized. Up to 60 wt.% CaO in steelmaking slag and up to 74.5 wt.% V<sub>2</sub>O<sub>5</sub> in petcoke ash were reported. Due to strong chemical affinity of calcium oxide to vanadium oxide when reacted

under certain conditions, the presence of calcium influences valence of vanadium and changes it from 3+ to 5+, forming calcium orthovanadate ( $3\text{CaO}\cdot\text{V}_2\text{O}_5$ ). The vanadate formation occurs by removing oxygen from the surrounding in the system, following the fundamental reaction:



Excess heat generated from the reaction ranges from 104 kJ to 163 kJ per mole of calcium vanadate at 1573 K [11], depending on  $x$  ( $x = 0 - 1$ ). The transformation is, thus, highly exothermic and expected to be capable of breaking down carbon dioxide and/or water molecules into carbon monoxide and/or hydrogen, respectively. In this work, in-situ experiments were conducted on a synthetic slag mixture based on calcium rich metallurgical slag and vanadium rich petcoke slag to investigate potential fuel production from waste gas stream containing  $\text{CO}_2$ .



**Figure 1: Availability of calcium oxide in metallurgical slags and vanadium oxide in petcoke ash. Shaded bars indicate ranges found while horizontal lines indicate single data points. Note vanadium content is typically reported as  $\text{V}_2\text{O}_5$  but exists as  $\text{V}_2\text{O}_3$  in gasification slag. (BF = blast furnace, BOF = basic oxygen furnace, EAF = electric arc furnace, LF = ladle furnace, OHF = open hearth furnace)**

## Experimental

10 g of synthetic slag of  $8.2\text{Al}_2\text{O}_3\text{-}24.7\text{CaO-}8.2\text{Fe}_2\text{O}_3\text{-}1.6\text{SiO}_2\text{-}57.3\text{V}_2\text{O}_3$  (by weight) in a high density alumina boat was heated from room temperature to 1773 K at 150 K/hr in a closed alumina tube. The slag composition was determined based on mixing of a metallurgical slag (Ca-rich) and gasification petcoke ash (V-rich) to maximize the  $\text{CO}_2$ -to- $\text{CO}$  (or  $\text{H}_2\text{O}$ -to- $\text{H}_2$ ) gas conversion and to promote the slag to melt. The atmosphere in the furnace tube was designed to be saturated with  $\text{CO}_2$  by using 0.07 g of carbon powder to react with oxygen present in the sealed air during the heating stage. The carbon quantity was determined so that no elemental

carbon would remain from the reaction. The electromotive force (EMF) inside an yttria-stabilized zirconia oxygen sensor (SIRO<sub>2</sub><sup>®</sup> - Ceramic Oxide Fabricators, Australia) was continuously measured, which was converted to oxygen partial pressure. An experimental error of the oxygen sensor was reported to be  $\pm 0.2$  log units between 1273 and 1773 K for  $10^{-5}$  –  $10^5$  Pa [12]. Concentrations of CO and CO<sub>2</sub> in the atmosphere in the tube were determined by thermodynamic computational software, FactSage 6.4 with FactPS and FToxid databases [13] based on the empirical oxygen potentials. Note that due to a lack of a slag database containing vanadium oxide in FactSage, V<sub>2</sub>O<sub>3</sub> solubility in the slag was assumed to be negligible. Creation of a database for slag containing vanadium is currently underway [6, 14]. The test was performed a second time for reproducibility, and was conducted with and without the slag to ensure no effect of carbon on oxygen potentials during CO<sub>2</sub> conversion.

## Results and Discussion

EMF measurements for the CO<sub>2</sub> saturated atmosphere sealed inside the reaction tube during the tests are presented in Figure 2. Time in the figure was adjusted for simplification purposes (*i.e.*, 1500 K starts at 0 min). The EMF without the slag (test 0) remained relatively constant between 1373 and 1773 K, with an average oxygen partial pressure of  $5 \times 10^3$  Pa. This agrees with a theoretical value of  $2 \times 10^3$  Pa determined by FactSage. Rapid increases in the EMF at approximately 55 min in Figure 2 c) correspond to sudden drops in the oxygen partial pressure caused by the slag interacting with CO<sub>2</sub> being converted to CO. First derivatives of the EMF with respect to time ( $dEMF/dt$ ) for tests 1 and 2 are shown in Figure 2 d). The CO<sub>2</sub>-to-CO conversion was rapidly initiated at 1695 – 1703 K, and the majority of the reaction was completed within 5 min. A minimal decrease in the oxygen partial pressure (*i.e.*, increase in EMF) was noted after the rapid conversions. The oxygen partial pressure determined from the EMF reached near-asymptotes of  $2 \times 10^{-5}$  –  $5 \times 10^{-5}$  Pa as heating continued. The result indicated a CO<sub>2</sub> conversion rate of 97% (to CO). The formation of (CaO)<sub>3</sub>V<sub>2</sub>O<sub>5</sub> was confirmed by X-ray diffraction analysis (Rigaku Ultima IV) on the quenched slag, implying the CO<sub>2</sub>-to-CO conversion was triggered by the vanadate formation (involving a valence change from V<sup>3+</sup> to V<sup>5+</sup>).

Computational thermodynamic simulations by FactSage suggested that if the same slag methodology is applied to water instead of carbon dioxide, H<sub>2</sub> would be produced following reaction (1). An oxygen atom is stripped off from a H<sub>2</sub>O molecule when CaO and V<sub>2</sub>O<sub>3</sub> react to form (CaO)<sub>3</sub>(V<sub>2</sub>O<sub>5</sub>), leaving H<sub>2</sub> as a byproduct. Theoretically, up to 1 ton of H<sub>2</sub> gas would be generated from the reaction with slag containing 4.2 tons of V<sub>2</sub>O<sub>3</sub>. Because H<sub>2</sub> is generated from the highly exothermic reaction, the H<sub>2</sub> conversion rate would be significantly greater than that from the traditional thermal dissociation routes where heat is supplied by recovering from the discharged slag in iron and steelmaking.

When the calcium vanadate forms in the molten slag, the density of the bulk slag increases from 1.12 g/cm<sup>3</sup> [15] to 3.96 g/cm<sup>3</sup> [16], which in turn decreases the slag volume to approximately 30 % of the original volume per unit mass. The volume reduction of the final slag would help conserve landfill sites as required for the current slag disposal in industries.

A larger scale test to examine the practicality of the process is underway. The effect of preparation and chemistry modification of slags, as well as timing of mixing the two slags will be investigated to maximize the generation of heat and syngas ( $H_2$  and  $CO$ ).

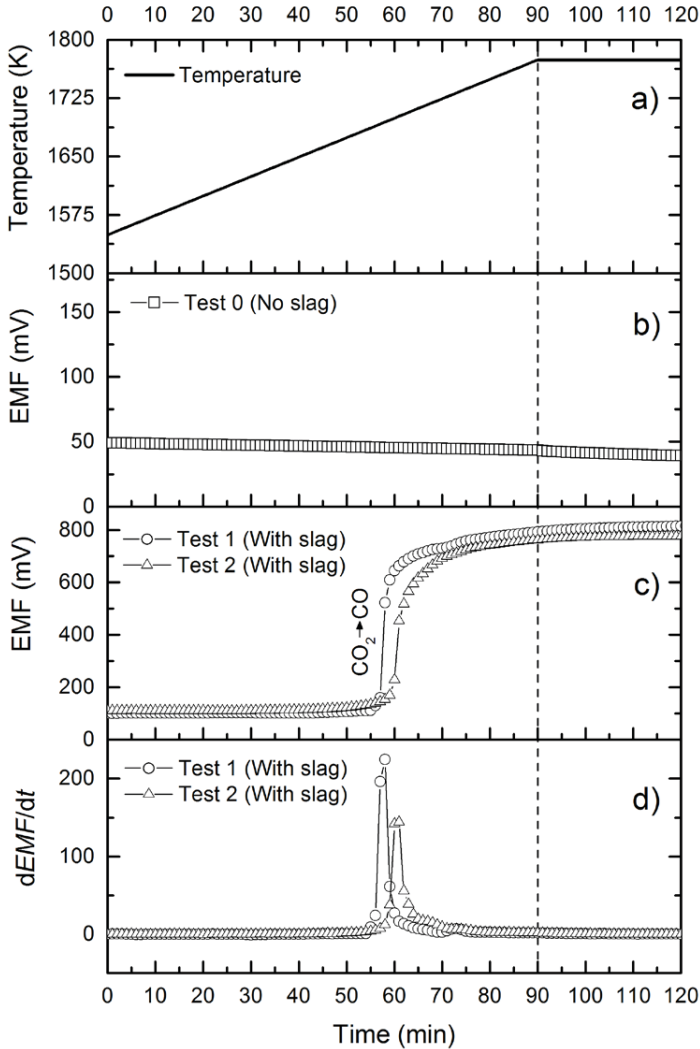


Figure 2: In-situ measurements of a) temperature inside the tube and EMF of b) without the present slag, c) first and second tests with the present slag mixture, and d) the first derivative of the EMF ( $dEMF/dt$ ) of first and second tests.

## Conclusion

Synthetic iron & steelmaking and gasification slags mixed at a specific composition were heated at a slag discharge temperature range in the presence of CO<sub>2</sub>, resulting in production of CO due to the formation of calcium orthovanadate. Computational simulations suggested that H<sub>2</sub> would be generated from H<sub>2</sub>O using same mixed slag approach. The final slag volume would decrease to about 30% of the original volume, lightening burden imposed on landfill sites. The present research result would suggest a potential approach to reduce current environmental loads while commercially benefitting metallurgical and gasification industries.

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