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Supplementary Material

Replacing Fossil Carbon in the Production of Ferroalloys with a Focus on Bio-Based Carbon: A Review

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1. Partial Pressure to Reduce Metal Oxides

As shown in Figure 1 of the full article, the Gibbs free energy for the pre-reduction and reduction of metal oxides by hydrogen is higher than the same reaction using carbon as a reducing agent. However, Figure 1 has the limitation, that the pressure of hydrogen, carbon monoxide and water vapor is set to be one. By decreasing the partial pressure of the product gas, it can be possible that the pre-reduction and reduction reactions occur using hydrogen as a reducing agent. Using Equation (1), it is possible to derive an equation to calculate the partial pressure of CO and the ratio of the H_2O and H_2 partial pressure at equilibrium.

$$\Delta_r G = 0 = \Delta_r G° + RT \ln(K) \quad (1)$$

$\Delta_r G$: Gibbs free energy in J/mol; $\Delta_r G°$: Gibbs free energy (1 atm) in J/mol; R: Gas constant in J/mol; T: Temperature in K; K: Equilibrium constant; p_x: Partial pressure of x in atm

As a first assumption, it is necessary to assume an activity of 1 for the condensed phases to simplify the equilibrium constant. This will result in Equation (2) for the reduction with hydrogen and Equation (3) for the reduction with carbon.

$$\Delta_r G = 0 = \Delta_r G° + RT \ln\left(\frac{p_{H_2O}}{p_{H_2}}\right) \quad (2)$$

$$\Delta_r G = 0 = \Delta_r G° + RT \ln(p_{CO}) \quad (3)$$

Equation (2) and (3) can be rewritten as Equation (4) and (5) to calculate the partial pressures of interest.

$$\frac{p_{H_2O}}{p_{H_2}} = e^{-\frac{\Delta_r G°}{RT}} \quad (4)$$

$$p_{CO} = e^{-\frac{\Delta_r G°}{RT}} \quad (5)$$

Using the Gibbs free energy presented in Figure 1 of the article, it is possible to calculate the partial pressures. Figure S1 shows the equilibrium partial pressure of relevant reactions for pre-reduction or reduction for metal oxides of nickel, iron, chromium, manganese and silicon covered by this review.

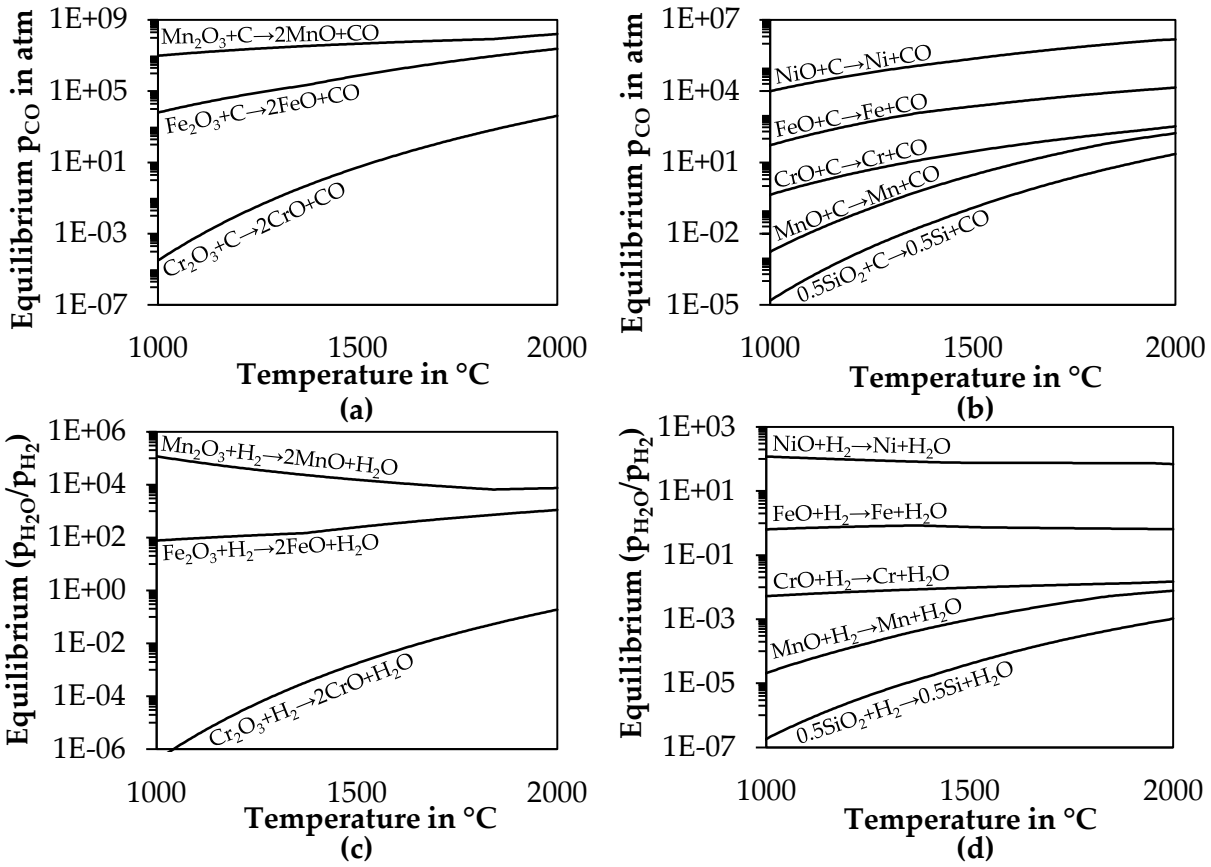

Figure S1. Equilibrium partial pressure of CO and equilibrium H_2O to H_2 ratio for the selected reduction reactions. (**a**) pre-reduction with carbon; (**b**) reduction with carbon; (**c**) pre-reduction with hydrogen; (**d**) reduction with hydrogen.

As already mentioned in the article, the reduction of CrO, MnO and SiO_2 will require a very low ratio of the H_2O to H_2 partial pressure. However, the equilibrium partial pressure ratio for the FeO reduction is reasonable and between 0.636 and 0.845.