

Possibilities and Limitations of the Use of Hydrogen in Different Metallurgical Sectors [†]

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Abstract: Hydrogen is increasingly being recognized as a crucial element in reducing carbon emissions in the metallurgical industry. Its use in the steel sector is gaining momentum through various initiatives at high TRL levels. Moreover, hydrogen shows promise in other metal production processes as well. One application involves utilizing hydrogen for effective selective reduction copper from copper slags with a low amount of iron being reduced. Hydrogen can also be employed in the pre-reduction of manganese ore, leading to the carbon-free production of manganese metal through aluminothermic reactions. Additionally, hydrogen can be used in the processing of bauxite residue, where iron is partially or completely reduced to separate an iron-rich fraction, allowing for alumina recovery via leaching.

Keywords: hydrogen; reduction; copper; manganese; slag



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1. Introduction

The metallurgical sector is vital to a sustainable future as vast amounts of metals, such as steel, aluminum, and copper are required for solar panels, wind turbines, electrification of transport and upgrading of the electricity grid. However, the metallurgical industry is also one of the largest CO₂ emitting sectors. Hydrogen is a key enabler for reducing carbon emissions in the metallurgical industry. It is being explored for use in processing bauxite residue [1], pre-reducing manganese ore, recovering copper from copper slags and as a fuel for heating in steel and aluminum production, replacing fossil fuel-based oxyfuel burners. These applications have the potential to make various metallurgical sectors more environmentally friendly.

2. Thermodynamics

Figure 1 presents the Ellingham diagram, which is essentially a graph plotting the free energy changes, ΔG° , against temperature. Given that the enthalpy changes, ΔH° , and entropy changes, ΔS° , remain virtually constant with temperature barring any phase changes, the free energy versus temperature plot can be represented as a sequence of straight lines. The Ellingham diagram serves two primary purposes: it facilitates the determination of the relative ease with which a specific metallic oxide can be reduced to its metal, and it enables the calculation of the partial pressure of oxygen in equilibrium with a metal oxide at a specified temperature.

The position of the line for a given reaction on the Ellingham diagram shows the stability of the oxide as a function of temperature. Reactions closer to the top of the diagram are the most “noble” metals (for example, copper and nickel), and their oxides are unstable and easily reduced. Moving down toward the bottom of the diagram, the metals become

progressively more reactive, and their oxides become harder to reduce. A given metal can reduce the oxides of all other metals whose lines lie above theirs on the diagram [2].

It is clear from the diagram that hydrogen is a less potent reductant than solid carbon. Oxides like Al-, Mn-, and Si-oxides cannot be completely reduced to metals using hydrogen only. Figure 1 also shows that the reduction of hematite to magnetite and manganese to wüstite is straightforwardly achieved using hydrogen but the driving force for the final reduction to iron metal is low so this final reaction from wüstite to iron is sluggish. Moreover, a gas atmosphere containing a high H₂/H₂O ratio is needed for the formation of iron metal.

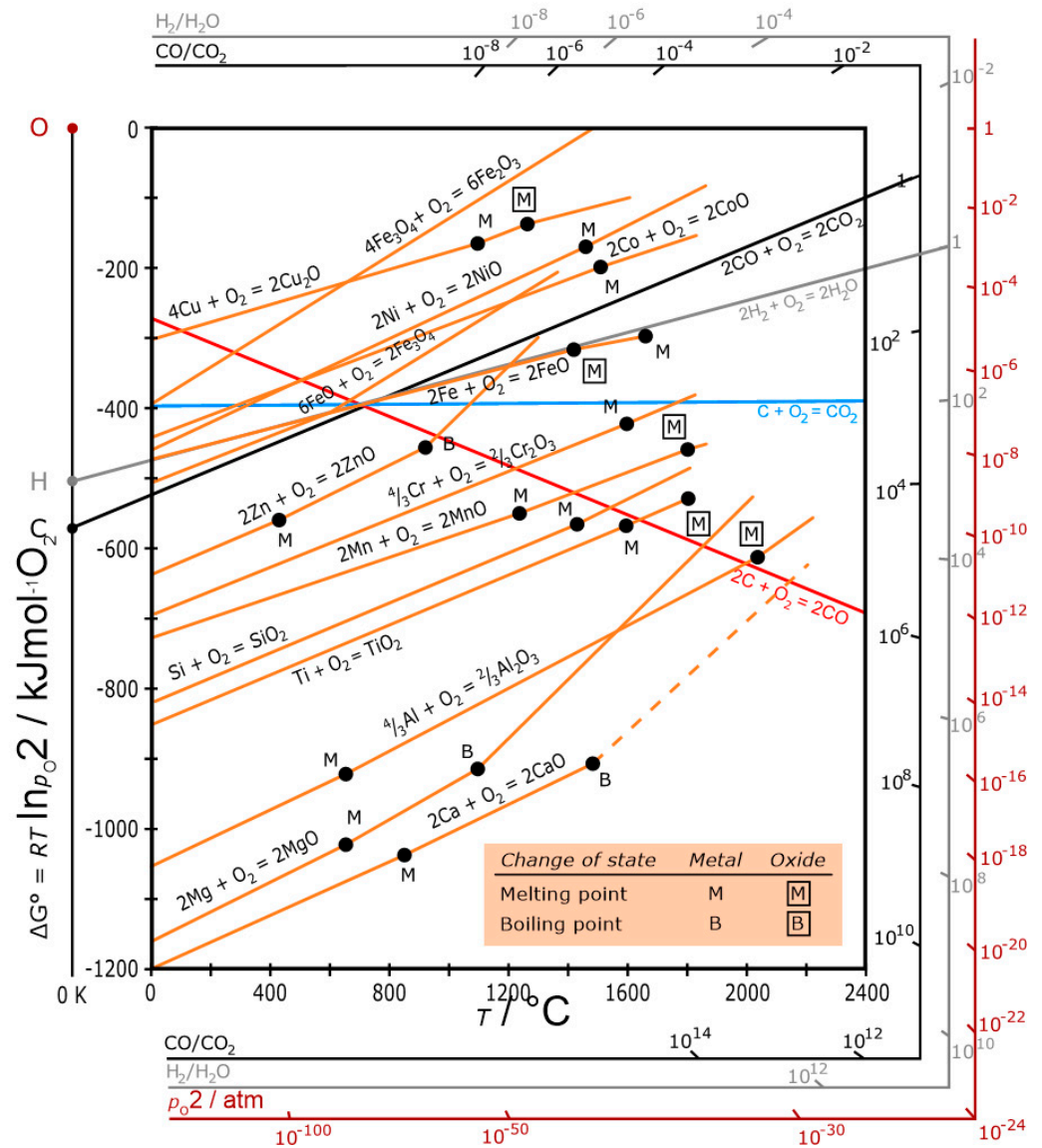


Figure 1. The Ellingham diagram [3].

3. Hydrogen Reduction Treatment of Copper-Containing Slags

Slag from copper flash smelting contains not only slag-forming components but also copper levels comparable to that in ores from modern mines (1~2 wt%). In addition, it contains iron oxide (~50 wt%), alkalis and heavy metals (K, Na, Zn, Pb++, ~3–5 wt%), as well as smaller amounts of molybdenum, cobalt and nickel. The high iron content of the slag makes it challenging with traditional methods to extract the copper without also extracting a lot of iron and creating a low-Cu high-Fe alloy of little commercial relevance. Even without copper recovery, the alkalis and heavy metals make it difficult to valorize the

slag as a construction material or as an iron source. The low-value options available for slag valorization are as a blast abrasion agent, cement compound and river embankment. The slag is partly valorized through these means, but volumes are limited. Furthermore, legal limits for heavy metals will be lowered in the future, further restricting the opportunities available [4,5].

Primary copper slag is produced by around 2–3 t per ton of copper, with concentrations of up to 2 wt.% Cu left inside after common cleaning processes. This copper can be recovered using hydrogen. Within the HARARE project [4,5], the process to recover copper is investigated. The selectivity of the hydrogen reduction, as illustrated in Figure 1, is the key to obtaining a metal phase with a high copper and low iron content.

Hovestad [6] has demonstrated hydrogen reduction of copper from primary, fayalitic slags. The initial copper content was between 0.9 and 2.0 wt.%, and the hydrogen concentration was set between 15 and 90 wt.%. The study found that with enough turbulence in the melt, the rate constant could be established as a linear function of hydrogen concentration. The current study confirms that the reduction of low concentration slags follows a first-order reaction, meaning that doubling the hydrogen concentration doubles the rate constant. The lowest final copper content in the slag achieved was 0.3 wt.%. The study also found that turbulence could enhance the reaction rate by up to 40%, implying that liquid transport is the time-determining step in the process.

Moreover, during the copper reduction, zinc and lead are evaporated due to the bubbling of hydrogen through the liquid slag. The evaporated zinc and lead will leave the melt and are oxidized again by the introduction of air. These oxides are then collected in a filter system. Hovestad [7] has shown that the process of fuming zinc and lead with hydrogen is effective. The performance of hydrogen appears to remain consistent across a broad spectrum of reduction gas concentrations, as evidenced by similar final Zn and Pb contents. As a result, increasing the hydrogen concentration could significantly reduce the processing time. The lowest lead and zinc contents achieved were 0.04 and 0.2 wt.% for primary slag and 0.02 and 0.49 wt.% for secondary slag, respectively. Zinc concentrations above a certain level appear to follow a linear trend, while those below 1 wt.% exhibit a declining rate of reduction. During the fuming process, the diffusion of zinc oxide in the slag phase appears to become increasingly significant.

4. Prereduction of Mn Ore with Hydrogen and Aluminothermic Reduction

Manganese, while not widely known by most people, is a metal of significant importance in our society. It holds the position of the fifth most utilized metal in terms of volume, trailing behind iron, aluminum, copper and magnesium [8]. The influence of manganese is felt in our everyday lives, whether through steel-made objects, batteries or aluminum beverage cans, among other things. It has been instrumental in the evolution of various steelmaking procedures, and its ongoing relevance is underscored by the fact that approximately 90% of all manganese used annually is dedicated to steel production. The primary method for manganese production is through carbothermic reduction of manganese ores in a submerged arc furnace (SAF), resulting in manganese ferroalloys such as high-carbon ferromanganese (HCFeMn). The production of HCFeMn through a carbothermic process in SAF is accompanied with significant CO₂ emission of about 1–1.4 t CO₂/t metal. On the other hand, the SAF process is an energy intensive process and 2000–3000 kWh energy is utilized per ton metal [8]. Therefore, the development of new sustainable Mn production processes is important to reduce the emission of greenhouse gases in the future. In a newly introduced integrated metallurgical process, which is called the HAlMan process, manganese and its alloys are produced through an approach in which the reduction of manganese oxides (MnO₂, Mn₂O₃ and Mn₃O₄) to MnO is carried out by hydrogen gas as the reduction of MnO to metallic Mn by hydrogen is not possible regarding the above Ellingham diagram. In the next step of the process, MnO is reduced to Mn via an

aluminothermic reduction process at elevated temperatures with lime use as flux [8]. The main chemical reactions in the HAlMan process are given in the following:



Figure 2 shows an illustration of the HAlMan process with three units of a pre-reduction reactor, smelting-reduction furnace and a gas treating unit. The hydrogen reduction of Manganese ore occurs in the pre-reduction reactor using hot hydrogen. As the above-related reduction reactions are exothermic, the generated heat in the reactor and the enthalpy of the hot hydrogen provides the required heat for the reactor, and hence a hot pre-reduced Mn ore is possible to be discharged. The advantage of the hot discharge is saving thermal energy in the smelting-reduction furnace. A hot process gas also leaves the reactor that contains a significant amount of hydrogen, and the hydrogen can be partially looped through the gas treating unit, while cold hydrogen is heated up to the required temperature for the pre-reduction reactor.

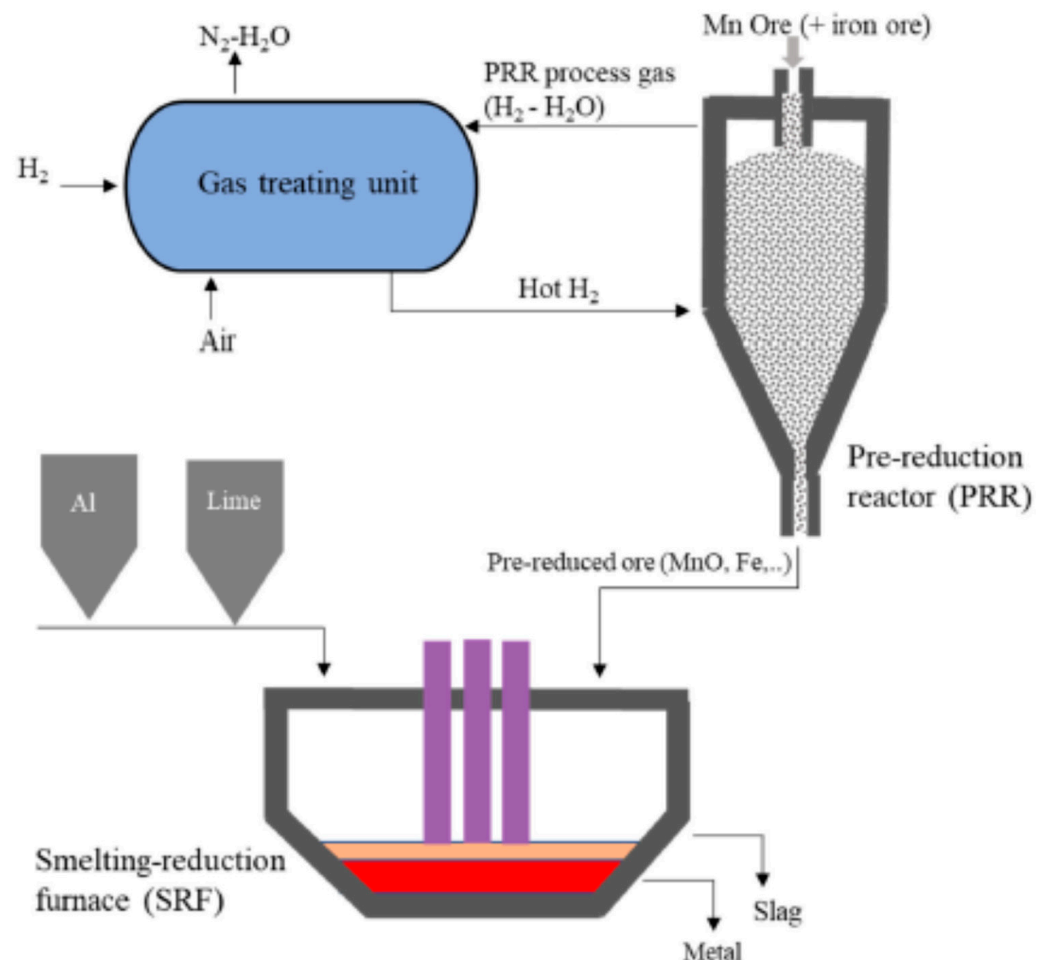


Figure 2. Schematic of the HAlMan process [9].

The pre-reduced Mn ore from the pre-reduction reactor contains manganese in the form of MnO and iron in the form of metallic Fe, as the Ellingham diagram in Figure 1

predicts. If the iron content of the Mn ore is not high enough, the addition of iron ore into the feed of the pre-reduction reactor will help to adjust the composition of the final metal product, or alternatively iron can be added in the smelting-reduction furnace [9]. The HALMan process is demonstrated at the pilot scale through an Innovation Action (IA) project in the Horizon Europe program within 2023–2026 [10]. The hydrogen reduction in manganese ores will be studied at the pilot scale in different technologies such as a hydrogen plasma rotary furnace, shaft reactor and vertical tube reactor.

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