MATERIAL CHARACTERIZATION AND SELECTION OF MANGANESE ORES FOR HYDROGEN-BASED REDUCTION PROCESSES

[1]Zuzana MIŠKOVIČOVÁ, [1]Jaroslav LEGEMZA, [1]Róbert FINDORÁK, [1]Peter DEMETER, [1]Branislav BUĽKO, [1]Jaroslav DEMETER

[1]TUKE FMMR - Technical University of Košice, Košice, Slovak Republic, EU, zuzana.miskovicova@tuke.sk

https://doi.org/10.37904/metal.2025.5107

Abstract

In light of the European Union's energy transition strategy aimed at minimizing dependence on fossil fuels, hydrogen has emerged as a key non-carbonaceous reducing agent, offering significant potential for application in metallurgical processes. This study focuses on the material characterization of selected high-grade manganese ores and evaluates their suitability for hydrogen-based reduction. The investigated samples originated from Burkina Faso, Gabon, Ghana, and South Africa—regions known for some of the highest-quality manganese deposits globally. Material testing included chemical, mineralogical, physical, and thermal property analyses, with an emphasis on reducibility. The effectiveness of hydrogen reduction largely depends on the oxidation state of manganese in the ores. Ores rich in MnO_2, such as those from Gabon, demonstrated the highest suitability due to the favorable reduction path to MnO. Gabonese ore, dominated by porous pyrolusite and with low SiO_2 content, showed promising characteristics for low-temperature hydrogen reduction (below 500 °C). In contrast, ores from South Africa and Ghana, which contain manganese primarily in carbonate form (rhodochrosite), exhibited lower potential for hydrogen-based processing. These ores are more suitable for carbothermal reduction, as the dissociation of $MnCO_3$ to MnO does not align with hydrogen reduction pathways. Overall, the study confirms that mineralogical composition—specifically the presence of higher manganese oxides—plays a critical role in determining the feasibility of hydrogen utilization in manganese ore reduction. The findings support the selection of specific ore types for further thermodynamic simulations and experimental work in the development of low-emission metallurgical technologies.

Keywords: Hydrogen-reduction, manganese ore, reduction treatment, mineralogical characterization

1. INTRODUCTION

The suitability of manganese ores for hydrogen-based reduction is primarily governed by their physicochemical and mineralogical properties. This study focuses on evaluating various manganese-bearing raw materials—such as lump ores, agglomerates, concentrates, pellets, and synthetic oxides—to determine their potential for low-emission hydrogen processing. Hydrogen reduction is most effective in ores containing manganese in higher oxidation states, particularly as pyrolusite (MnO_2), which offers favorable stability and reducibility. Reduction efficiency decreases in materials with elevated gangue content, while synthetic oxide powders demonstrate near-complete conversion under optimal conditions. Since manganese naturally occurs in both simple and complex oxide forms (e.g., pyrolusite, psilomelane, cryptomelane), understanding its mineral phase is essential to predicting reduction behavior [1]. Several studies confirm hydrogen's positive effect on manganese ore reduction. Schanche and Tangstad observed significantly enhanced kinetics in Nchwaning ore when hydrogen was added to the gas atmosphere, a finding supported by Ngoy et al [2]. Hydrogen is especially suitable for pre-reduction steps, converting MnO_2 and Mn_3O_4 to MnO. However, further reduction to metallic Mn requires the presence of carbon. At temperatures above 1000 °C, hydrogen can also reduce iron oxides, with both reduction rate and extent improving up to 1200 °C [3,4]. Nonetheless, high silica content in ores can hinder reduction by forming stable silicate phases, such as fayalite and tephroite. Ores from Groote Eylandt and Comilog have been identified as highly reducible due to their favorable composition and mineralogy. This is partly attributed to the fast reduction of intermediate bixbyite phases, unlike the slower kinetics seen in complex braunite-silicate ores [4]. Additionally, many manganese minerals deviate from ideal stoichiometry, often showing variable oxidation, hydration, or partial transformation to carbonates, which further impacts their reduction behavior. Although hydrogen offers environmental benefits as a carbon-free reductant, its application in industrial manganese processing remains at a developmental stage. Therefore, understanding ore-specific characteristics is crucial for designing efficient reduction pathways and integrating hydrogen into sustainable metallurgical operations [5]. This work provides a basis for selecting and optimizing manganese ores for future low-emission processing routes. Further experimental validation, including kinetic modeling and pilot-scale testing, is necessary to assess process viability under industrial conditions. Integrating hydrogen reduction with existing infrastructure also poses challenges in terms of energy input and gas supply. Nonetheless, targeted pre-reduction using hydrogen presents a promising pathway toward decarbonizing manganese metallurgy. Its success will depend not only on ore selection but also on controlling reaction environments and gas compositions. Continued research is essential to close the gap between laboratory findings and industrial-scale application.

2. MATERIALS AND METHODS

Values of bulk and true specific gravity were identified for all types of raw samples, while their average values correlated to their declared richness. Their chemical composition was identified by applying several methodologies prescribed by ISO, ASTM, and DIN standards as well as company standards. The methods applied mainly included X-ray fluorescence (XRF), atomic absorption spectroscopy (AAS), infrared spectroscopy (IR), and titration and gravimetry methods. Chemical composition was determined with a Niton XL3 Gold XRF spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) and using Thermo Scientific ICE 3500 AAS (Thermo Fisher Scientific, Waltham, MA, USA) elemental analysis. The Elemental Vario (Elementar Analysensysteme GmbH, Langen-selbold, Germany) was used for sulphur analysis. A sieve analysis was carried out using a vibration-pendulum sorting machine KVT-U-2 with a set of sieves. Phase analyses were performed using an X-ray diffraction analyser—D8 Advance, Bruker AXS (Karlsruhe, Germany), and the melting interval was identified by analysing images from a high-temperature microscope—Leitz WETZLAR (New York Microscope Company, New York, USA). For microscopic observation of the samples, a FE SEM MIRA 3 scanning electron microscope (TESCAN, Brno, Czech Republic) was used.Thermodynamic modelling was carried out using the thermodynamic software “HSC Chemistry”, versions 9 and 5.11, by Outokumpu Research Oy, Pori, Finland.

3. RESULTS AND DISCUSSION

The selection of manganese ore samples for experimental investigation was intentionally based on a diverse range of ore qualities in order to systematically evaluate the influence of compositional and mineralogical differences on their behavior under hydrogen reduction conditions. This approach enables the identification of correlations between ore characteristics and their reducibility, thereby allowing for a more accurate prediction of their suitability for hydrogen-based metallurgical processes.

Table 1 summarizes selected physicochemical and mineralogical properties of the tested manganese ores, which serve as the basis for further analysis and interpretation of their reduction behavior.

Table 1 Summary of the physicochemical properties of Mn ores

Manganese ore					
		Burkina Faso (Afrika)	**Gabon (Afrika)**	**Ghana (Afrika)**	**RSA (Afrika)**
Chemical composition (wt.%)	$\mathrm{Mn_{TOT}}$	52.05	53.09	37.73	34.32
	$\mathrm{Fe_{TOT}}$	0.94	1.39	1.13	14.35
	SiO_2	4.66	3.94	5.02	5.61
	Al_2O_3	2.97	6.70	1.52	0.42
	CaO	0.22	0.11	3.07	9.25
	MgO	0.07	0.09	4.43	3.01
	P	0.07	0.04	0.08	0.03
	S	0.04	0.03	0.12	0.21
	Na_2O	0.07	0.05	0.28	0.16
	K_2O	0.90	0.71	0.21	0.05
Granulometric composition (%)	< 5 mm	0.00	0.05	0.00	0.00
	< 10 mm	2.21	0.46	1.62	7.45
	< 20 mm	15.24	10.33	12.02	21.07
	< 40 mm	49.84	38.41	41.55	65.24
	< 80 mm	85.84	78.74	81.35	99.73
Apparent specific density ($g.cm^{-3}$)	ρ_A	2.65	2.61	2.03	2.12
True specific density ($g.cm^{-3}$)	ρ	5.05	4.78	3.65	3.72
Melting point (°C)		> 1550	> 1550	1470	1410
Mineralogical composition	XRD	pyrolusite, manganite, pyrochroite, quartz	pyrolusite, quartz, magnetite	rhodochrozite, quartz	rhodochrozite, braunite, quartz, hematite

Based on the results of physicochemical and metallurgical characterization of manganese ores, the Gabonese ore has been identified as the most suitable material for initial hydrogen reduction experiments, due to its superior overall quality. The total manganese content (Mn_total) in this ore reaches approximately 53 wt.%, with the majority of manganese present in the form of pyrolusite (MnO_2), which is a highly reducible manganese oxide.

Microscopic analysis of the Gabon ore reveals that the pyrolusite phase exhibits a porous microstructure. This porosity is of particular importance for gas–solid reduction reactions, as it enhances the surface area available for reaction and facilitates the diffusion of hydrogen into the interior of the ore particles. These microstructural characteristics are expected to positively influence the kinetics and overall efficiency of hydrogen-based reduction (See **Figure 1**).

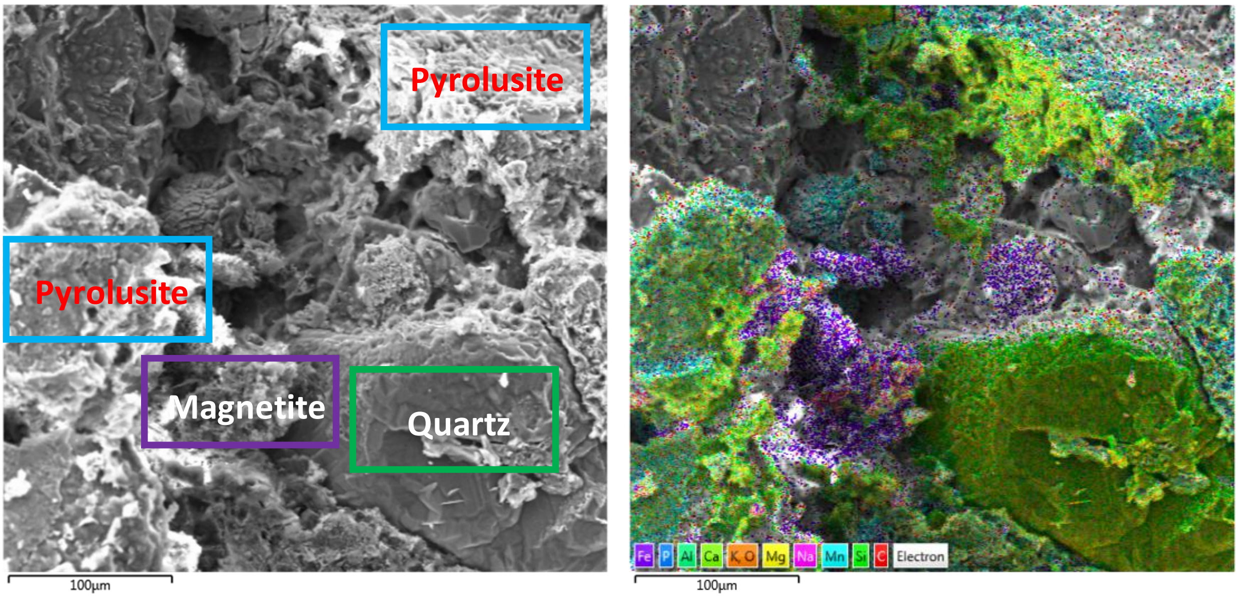

Figure 1 Microscopic analysis of Mn ore Gabon

In addition to its favorable manganese phase composition, the Gabon ore also contains the lowest proportion of SiO_2 among the analyzed samples. The silica is predominantly present as discrete quartz grains rather than being finely disseminated within the manganese matrix. This mineralogical feature is advantageous, as it minimizes potential interactions between silica and manganese during reduction, which could otherwise lead to the formation of undesirable silicate phases that inhibit reduction efficiency. The combination of high MnO_2 content, favorable porosity, and low silica content makes Gabon ore a prime candidate for hydrogen-based pre-reduction processes.

Conversely, the South African (RSA) ore represents the least favorable material for hydrogen reduction. It contains only 34.32 wt.% total manganese, accompanied by a relatively high SiO_2 content of 5.61 wt.%. The manganese in this ore is present primarily in the form of rhodochrosite ($MnCO_3$) and braunite-type silicates, such as $CaMn_{14}{}^{+}{}_{3}SiO_{24}$. These mineral phases are significantly less amenable to reduction by hydrogen under standard conditions. Rhodochrosite decomposes upon heating at relatively low temperatures—substantially lower than those required for hydrogen reduction of Mn oxides—resulting in the formation of MnO. However, MnO is thermodynamically stable and not readily reducible by hydrogen in practical temperature ranges, thus making the rhodochrosite-bearing ores unsuitable for direct hydrogen reduction routes.

The physical characteristics of the analyzed manganese ores—specifically specific gravity, granulometric distribution, and melting point—offer also valuable insights into their suitability for hydrogen-based reduction processes. Ores from Gabon and Burkina Faso demonstrate favorable physical characteristics for such processing routes. Their high true specific densities suggest a dominant presence of manganese oxides in higher oxidation states, particularly pyrolusite, which is thermodynamically preferred for hydrogen reduction. The observed granulometric distribution indicates a well-developed particle size range that supports effective gas–solid interactions, while the high melting points confirm their structural stability under elevated temperatures typical for reduction conditions.

It should be emphasized that the application of hydrogen as a reducing agent in manganese metallurgy is most effective for the pre-reduction of higher manganese oxides (e.g., $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4$), as part of decarbonizing strategies aimed at reducing CO_2 emissions in ferroalloy production processes. Therefore, ores with a high content of Mn in higher oxidation states (particularly as MnO_2) and minimal inert gangue components are ideal for such applications. Rhodochrosite-rich manganese ores, such as those from Ghana and South Africa, although unsuitable for hydrogen-based reduction, may still be considered high-quality raw materials for conventional carbothermic processes, such as in the production of ferromanganese (FeMn).

The reduction behavior of manganese oxides with hydrogen across the temperature range of 0–1500 °C is characterized by a series of thermodynamically favorable stepwise reactions. The diagram (**Figure 2**) illustrates that the most favorable (i.e., thermodynamically downhill or spontaneous) reaction in the studied interval is the reduction of MnO_2 to Mn_3O_4. This is followed in descending order of favorability by the reductions: MnO_2 to Mn_2O_3, Mn_2O_3 to Mn_3O_4, MnO_2 to MnO, and Mn_2O_3 to MnO. All of these reactions proceed without thermodynamic constraints across the full evaluated temperature range, indicating their high potential for practical application in hydrogen-based pre-reduction. Notably, direct reduction of manganese oxides to metallic Mn does not occur spontaneously within the studied temperature interval. Metallic manganese can be reduced using atomic hydrogen, e.g. in a plasma furnace, **Figure 2**. Therefore, full metallization is not achievable under low-temperature hydrogen reduction conditions, and the process should be understood as a pre-reduction route primarily leading to MnO formation.

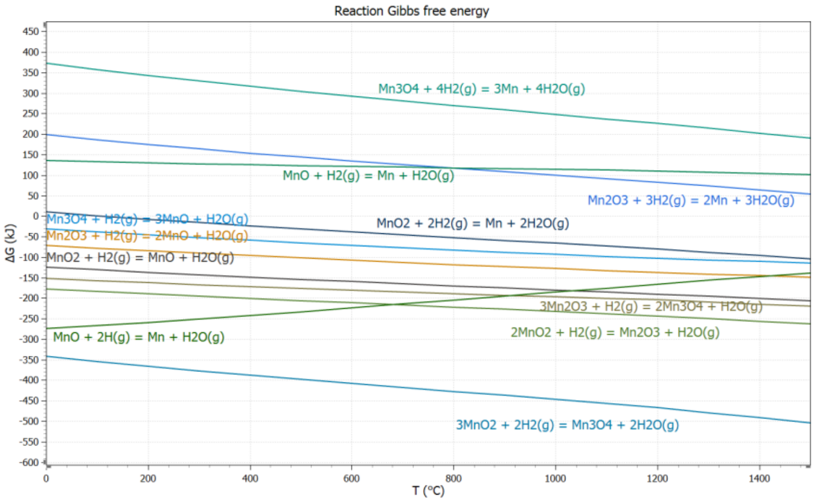

Figure 2 Thermodynamic simulations of hydrogen reduction potential of Manganese oxides

In support of this, **Figure 3** quantifies the hydrogen demand required for the complete reduction of pyrolusite (MnO_2) to MnO at 500 °C. The reaction stoichiometry and energy balance indicate that approximately 2.3 kg of hydrogen is needed to reduce 100 kg of MnO_2 to MnO. This data highlights the importance of accurate control over hydrogen dosage during reduction, both from a process efficiency and economic standpoint. These findings demonstrate that hydrogen-based reduction is particularly effective for the transformation of higher manganese oxides, such as MnO_2 and Mn_3O_4, to MnO. This stepwise reduction pathway is both thermodynamically feasible and kinetically advantageous, especially under controlled conditions relevant to industrial pre-reduction. The use of hydrogen in this context allows for a substantial reduction in carbon-based reductants and associated CO_2 emissions, aligning with current goals for cleaner metallurgical processing. As such, hydrogen-assisted pre-reduction represents a viable and sustainable approach within modern manganese production technologies.

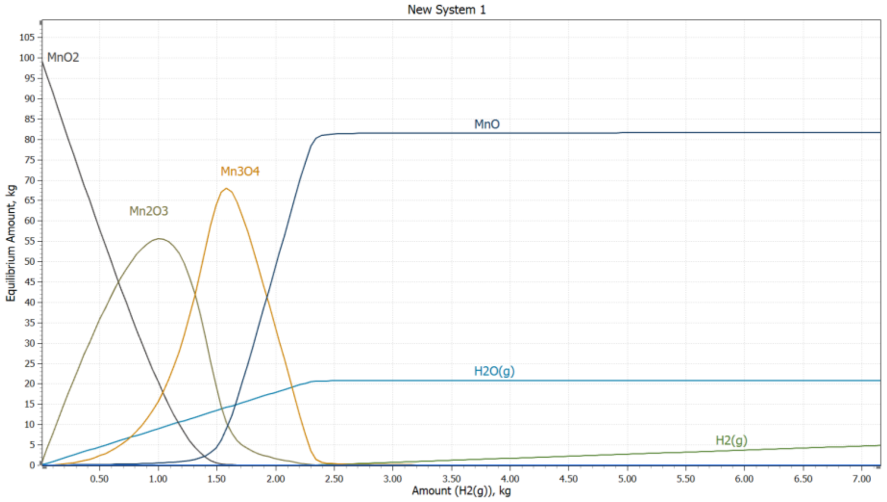

Figure 3 Effect of Hydrogen Quantity on the Reduction of Pyrolusite (MnO_2) at 500 °C

4. CONCLUSION

Based on a comprehensive evaluation of chemical, mineralogical, physical, and thermal properties, a preliminary selection of manganese ores was conducted to determine their suitability for hydrogen-based reduction. Ores rich in higher manganese oxides—particularly the Gabonese ore with dominant pyrolusite—were identified as the most favorable due to their high reducibility, low gangue content, and thermal stability. In contrast, Ghanaian and South African ores, containing manganese mainly in carbonate and silicate forms, were found less suitable for hydrogen reduction but remain appropriate for carbothermic routes. Thermodynamic modeling confirmed the favorable stepwise reduction of Mn oxides to MnO. These findings form a foundation for further experimental work aimed at developing low-emission manganese processing technologies**.**

ACKNOWLEDGEMENTS

This research was funded by the Slovak Research and Development Agency (APVV), Slovak Republic, No. APVV-21-0142 and VEGA ME SR AND SAS grant number - 1/0199/24.

REFERENCES

[1] NGOY, Didier et al. Pre-reduction Behaviour of Manganese Ores in H_2 and CO Containing Gases. *ISIJ International*. 2020, vol. 60, issue 11, pp. 2325–2331. DOI: 10.2355/isijinternational.ISIJINT-2020-120

[2] SCHANCHE, T. L.; TANGSTAD, M. Prereduction of Nchwaning Ore in $CO/CO_2/H_2$ Gas Mixtures. *Minerals*. 2021, vol. 11, issue 10, article 1097. DOI: 10.3390/min11101097.

[3] KONONOV, R.; OSTROVSKI, O.; GANGULY, S. Carbothermal Solid State Reduction of Manganese Ores: 2. Non-isothermal and Isothermal Reduction in Different Gas Atmospheres. *ISIJ International*. 2009, vol. 49, issue 8, pp. 1107–1114. DOI: 10.2355/isijinternational.49.1107.

[4] GRYC, K.; STROUHALOVÁ, M.; SMETANA, B.; SOCHA, L.; MICHALEK, K. Influence of Direct Thermal Analysis Experimental Conditions on Determination of the High Temperature Phase Transformation Temperatures. *Archives of Metallurgy and Materials*. 2015, vol. 60, issue 4, pp. 2867–2871. DOI: 10.1515/amm-2015-0458.

[5] BRUSTAD, O. K.; LÅSTAD, J.; HOSEINPUR, A.; SAFARIAN, J. Characterization, Calcination and Pre-Reduction of Polymetallic Manganese Nodules by Hydrogen and Methane. *Metals*. 2022, vol. 12, issue 12, article 2013. DOI: 10.3390/met12122013.