STUDY OF THE ISOTHERMAL PRE-REDUCTION BEHAVIOR OF COMILOG MANGANESE ORE UNDER THE H_2 ATMOSPHERE

Alok Sarkar[1], Maria Wallin[1] and Jafar Safarian[1]
1-Department of Materials Science and Engineering, Norwegian University of Science and Technology, Alfred Getz Vei 2, 7491 Trondheim.
Corresponding author's e-mail address: alok.sarkar@ntnu.no

ABSTRACT
Employing hydrogen as a reducing agent in ferromanganese production offers a promising and sustainable approach to achieve decarbonization within the ferroalloy industry. In the HAlMan EU project, this method is extensively researched and tested, ranging from laboratory to pilot scale. This study examines the impact of hydrogen on the pre-reduction of high-grade Comilog ore sourced from Gabon, Africa. Experimental investigations were carried out in a laboratory-scale vertical thermogravimetric furnace under isothermal conditions at temperatures of 600°C, 700°C, 800°C, and 900°C. The ore and reduced samples were subjected to comprehensive characterization utilizing XRF, XRD, ICP-MS, BET, Porosity, Pycnometry, EPMA, and SEM techniques, elucidating the hydrogen reduction behavior from mineralogical, microstructural, and chemical standpoints. Continuous monitoring of mass changes during reduction facilitated the assessment of both the rate and extent of the reduction process. The experimental results showed that the manganese and iron oxides in the Comilog ore are primarily in the form of MnO_2 (Pyrolusite) and Fe_2O_3 (hematite). The reduction rate in this ore is significantly higher compared to other manganese ores such as Nchwaning Mn ore due to its highly porous nature. Pre-reduction at different temperatures led to the creation of metallic iron (Fe) from Fe_2O_3 and the formation of manganese II oxide (MnO) from MnO_2. The pre-reduction temperature had an impact on the ore's pore structure, leading to notable changes in porosity.
Keywords: Hydrogen reduction, Thermogravimetry, Pre-reduction, Isothermal, Ferromanganese, Decarbonization.

INTRODUCTION
The primary technique currently employed in the production of manganese metal revolves around the carbothermic reduction process of manganese ore within submerged arc furnaces (SAF). In this process, metallurgical coke functions as both the main energy source and the agent for reduction, typically consuming around 2 tons per ton of alloy generated. This approach is characterized by its high energy consumption, requiring 2000–3000 kWh per ton of metal produced and emitting 1-1.4t CO_2 per ton of metal manufactured [1][2]. In alignment with the Paris Agreement objectives, there exists a goal to slash CO_2 emissions by 45% by 2030, with a subsequent aim for achieving net-zero emissions by 2050 [3]. The strategic vision outlined by the Norwegian process industries envisions "Combining growth and achieving zero emissions by 2050" as a key approach toward fulfilling these environmental targets [4]. Therefore, the development of new sustainable Mn production processes is important to reduce greenhouse gas emissions in the future. The HAlMan process is based on the idea of using hydrogen to reduce Mn oxides to MnO in a pre-reduction step in which the chemical reactions (1) to (3) occur. Then, the aluminothermic reduction of the pre-reduced ore (or MnO-containing material) is done to produce Mn metal, aluminum-manganese alloys (AlMn) and ferromanganese alloys through the reaction (4) [5].

$$2MnO_2(s)+H_2(g)= Mn_2O_3(s)+H_2O(g) \quad \Delta H_{(25°C)}= -163.7 kJ/mol \quad (1)$$
$$3Mn_2O_3(s)+H_2(g)= 2Mn_3O_4(s)+H_2O(g) \quad \Delta H_{(25°C)}= -135.1 kJ/mol \quad (2)$$
$$Mn_3O_4(s)+H_2(g)= 3MnO(s)+H_2O(g) \quad \Delta H_{(25°C)}= -16.6 kJ/mol \quad (3)$$
$$3MnO(s)+2Al(s)= 3Mn(l)+Al_2O_3(l) \quad \Delta H_{(25°C)}= -520 kJ/mol \quad (4)$$

METHODOLOGY
Figure 1 presents a summary of the method approach.

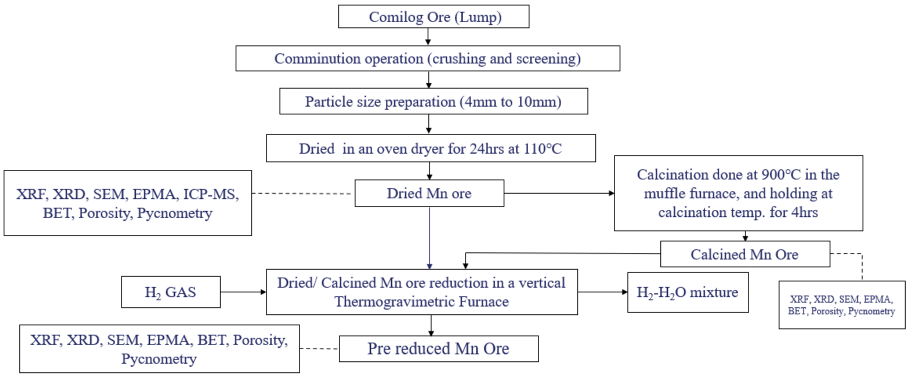

Figure 1: Flowsheet of the applied process and materials analysis of various products.

RESULTS AND DISCUSSION

Figure 2 depicts the pre-reduction characteristics under H_2 atmosphere of dried and calcined Comilog manganese ore across temperatures of 600°C, 700°C, 800°C, and 900°C, maintaining a constant reduction duration of 120 minutes with a sample weight of 150 grams. The dried pre-reduced sample exhibits the highest weight reduction of 19.35% at 900°C, whereas the pre-calcined sample at the same temperature displays a maximum weight reduction of 8.80%. These maximum weight reductions closely align with the theoretical maximum mass loss percentage at this temperature, indicating complete reduction at this temperature level. The lower weight reduction observed for the calcined ore is attributed to the removal of CO_2 from the carbonate materials during the calcination process, resulting in a lower achievable maximum weight reduction compared to the dried ore.

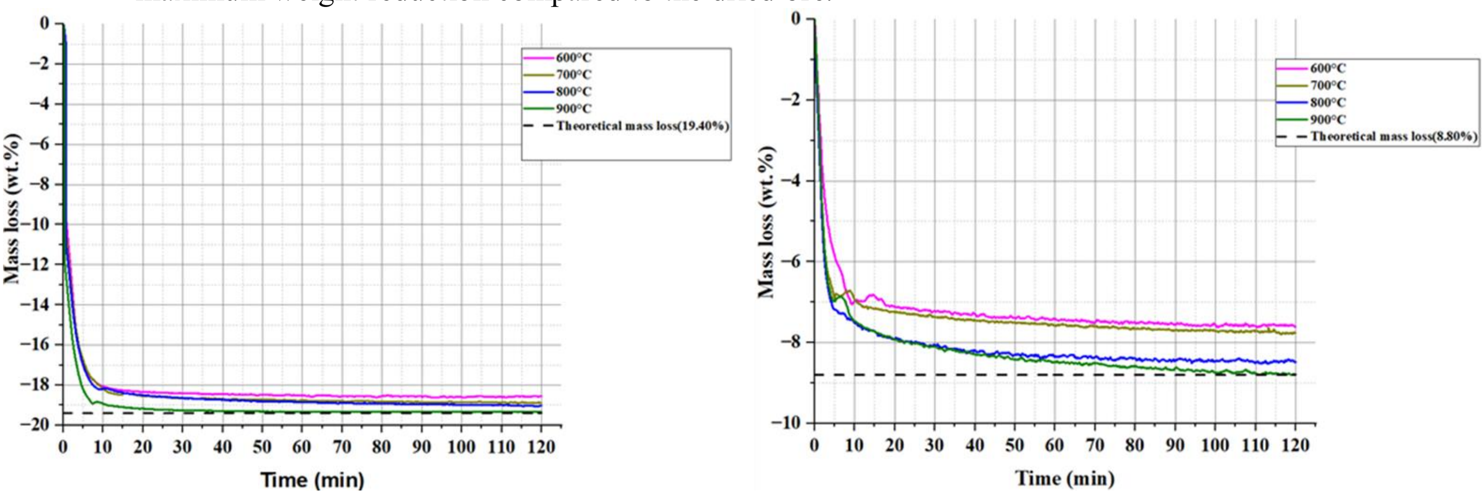

Figure 2: Mass loss (wt.%) vs. time (min) plot during H_2 reduction of the dried and pre-calcined samples

CONCLUSIONS:

The key findings of this study can be summarized as follows:

- The kinetics of the Comilog ore reduction with hydrogen are temperature dependent. Higher temperatures lead a faster and more extensive reduction.
- The raw Comilog ore exhibits notably higher porosity (20.68%) compared to other manganese ores like Nchwaning ore (Porosity: - 0.59%).

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