Update of the Manganese pathway in GREET® 2021

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ACRONYMS

BEV	battery electric vehicle
EV	electric vehicle
EMM	electrolytic manganese metal
HPEMM	high purity electrolytic manganese metal
HPMSM	high purity manganese sulfate monohydrate
LCA	life cycle analysis
LIB	lithium-ion battery
LMO	lithium manganese oxide
MSM	manganese sulfate monohydrate
NMC	lithium nickel manganese cobalt oxide
PHEV	plug-in hybrid vehicle

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This memo documents updates in the GREET® model for the manganese pathway.

1. Introduction

Manganese is considered an essential element for industrialized economies due to its use in almost all types of steel, as well as in chemical, agricultural, pharmaceutical and energy storage industries. Manganese is the twelfth most abundant element in the earth's crust and the fifth most mined metal by tonnage. The United States Geological Survey (USGS) reported the global reserves of manganese to be about 1.3 billion metric tons, and an annual global consumption of 18.5 million metric tons in 2020 [1]. According to USGS, South Africa accounts for about 78% of the world's identified manganese resources, while Ukraine accounts for about 10% [1]. Industrial utilization of manganese can be broadly divided into two: metallurgical and non-metallurgical application. Metallurgical application for steel production, either directly in pig iron manufacture or indirectly through upgrading the ore to ferroalloys accounts for most of the overall manganese ore consumption [1]. Non-metallurgical applications includes use in the cathode of batteries as well as in making specialty products and chemicals such as electrolytic manganese metal (EMM) used in aluminum alloys and manganese sulfate monohydrate (MSM) that is used as a fertilizer. Electrolytic manganese dioxide (EMD) that is used in batteries such as alkaline batteries, lithium manganese oxide (LMO) lithium-ion batteries (LIB) is also a non-metallurgical application of manganese. Figure 1 shows the manganese market share with utilization of manganese ores as silico-manganese, ferro-manganese, refined ferro-manganese and slag accounting for the metallurgical application of manganese.

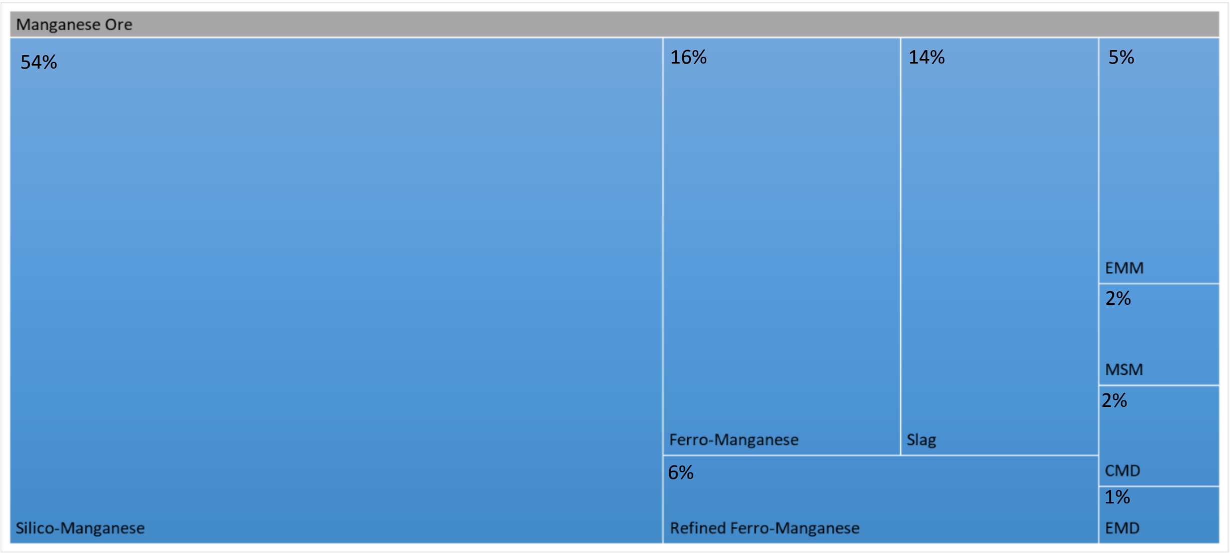

Figure 1. Manganese market share *(EMM denotes electrolytic manganese metal, MSM denotes manganese sulfate monohydrate, CMD denotes chemical manganese dioxide, and EMD denotes electrolytic manganese dioxide)

Recently, non-metallurgical application of manganese has been in the lithium nickel manganese cobalt (NMC) LIBs. The NMC LIB is the preferred LIB chemistry for many automakers for their battery electric vehicles, with the exception of Tesla. The NMC LIB utilizes manganese in the form of high purity manganese sulfate monohydrate (HPMSM). In 2017 (Figure 1), 17% of MSM was from HPMSM while 2.5% of EMM was from high purity electrolytic manganese metal (HPEMM) that was further processed into HPMSM. The use of manganese in LIBs is projected to increase significantly because of the projected increase in the adoption of electric vehicles powered by NMC LIBs and coupled with some automakers exploring manganese-rich LIBs.

Manganese is mainly obtained from either its carbonate (rhodochrosite) or oxide (pyrolusite) ores. HPMSM for application in LIBs of EVs can be produced from either ores through two main pathways. One of these ways is through a direct ore processing route that involves beneficiation, leaching, precipitation, crystallization, and drying to produce HPMSM. The other pathway involves first producing HPEMM through a number of steps that involves beneficiation, leaching, precipitation, and electrowinning. Though the production route using HPEMM is considered to be the easier route, it is a costlier route due to the high electricity intensity associated with the electrowinning step [2]. The more difficult direct route that entails chemical refining of the ore has been the preferred route by for HPMSM producers in China [2]. However, the high demand for HPMSM has led to the increasing utilization of the HPEMM route for the production of HPMSM. Talbot and Watts reported that some HPMSM producers in China are utilizing the HPEMM pathway because the direct ore processing route relies on the feedstock quality [3]. Most HPMSM production in the pipeline outside China such as in Europe and Australia are examining the HPEMM pathway for the production of HPMSM [3, 4]. In summary, the economic viability of the different pathways is influenced by factors such as cost and access to electricity, cost of acid, access to infrastructure, soluble manganese grade, ore impurities and metallurgy [5]. This update of the manganese pathway in GREET 2021 aims to add the production of HPMSM form HPEMM in line with the anticipated utilization of this route to meet the project increase in demand for HPMSM for EV applications.

It is worth to noting that while both carbonate and oxide ores can be utilized in the two pathways to produce HPMSM, however the oxide ore is insoluble in sulfuric acid. Therefore, it undergoes a calcination step to make it soluble prior to being leached with sulfuric acid. A simplified pathway to produce HPMSM from HPEMM is shown in Figure 2.

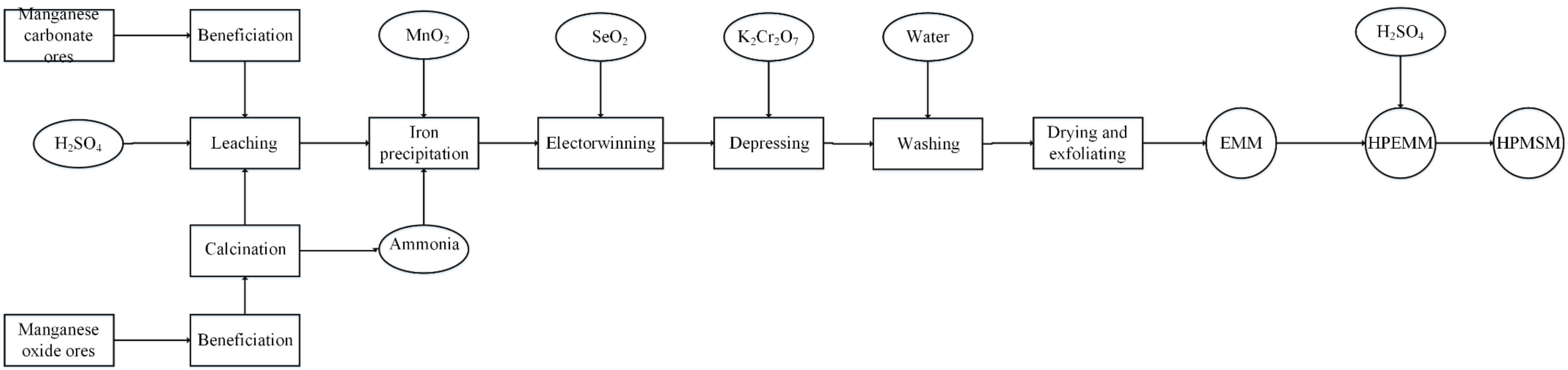

Figure 2. HPMSM production from carbonate and oxide ores of manganese through the HPEMM pathway

2. Updated Manganese Pathway

2.1. Direct ore processing pathway

The quality of the manganese ore being processed for the production of manganese through the direct ore processing route was updated from 55% to 35% in GREET 2021. Recent literature has shown that some manganese ores in countries like Brazil, India, and Gabon may have high manganese content that is higher than 40%. However, South Africa, which has the highest identified manganese resources, typically has ores with average ore grade of about 35%. The update to the manganese content of the ore for the direct ore processing was therefore updated to reflect this.

2.2. High Purity Electrolytic Manganese Metal pathway

The HPEMM pathway added to GREET 2021 is based on data from literature as shown in Table 1. It is worthy to note that the material and energy inputs shown in Table 1 produces EMM with a manganese content of about 99.7% and not the desired HPEMM with a manganese content of about 99.9%. Therefore the emissions calculated here will most likely underestimate the potential emissions for HPEMM production. The three different literature shown in Table 1 utilize manganese carbonate as the starting feedstock. Production of EMM in China has largely been from carbonate ores though tightening environmental regulation in China is leading to an increase in interest in utilizing oxide ores that results in less solid waste when compared with carbonate ores. Material and energy flows from literature show comparable values for most of the inputs to produce EMM has shown in Table 1. However, for this update, we used the inputs from the work of Zhang et. al [6].

Table 1. Reported material and energy inputs for EMM production

Input	Duan[7]	Hagelstein[8]	Zhang[6]
Manganese content in ore, %	16	<20	19.26
Manganese ore, tonne	8.68	8.68	7.81
Electricity, kWh	6800	7000	7385
H_2SO_4, tonne	1.96	2.2	0.8
Ammonia, tonne	0.11	0.08	0.06
Coal, tonne	-	-	0.83
Crude oil, kg	-	-	0.43
Fresh water, tonne	4.41†	69†	4.24
Tap water, tonne	-	-	0.25
SeO_2, kg	0.8 - 1.2	2.1	1.1
$K_2Cr_2O_7$, kg	0.1 - 0.3	-	0.57
$CaCO_3$, kg	-	-	9.07
MnO_2, tonne	0.76	-	-
Explosive, kg	-	-	0.65
Output			
Electrolytic Manganese Metal (EMM), tonne	1	1	1
Manganese content in EMM, %	99.7	99.7	

† Duan and Hagelstein simply reported the water requirements and did not distinguish whether it is tap or fresh water.

We chose the data from Zhang et. al because it is the most recent of this literature may be more in line with current production technology for EMM. Also, their data is from the leading producer of global EMM, accounting for about 40% of the market share of global EMM production and can therefore be considered an important production route for EMM.

The life cycle inventory data to produce EMM in GREET 2021 adapted from Zhang et. al is shown in Table 2. It is worth noting that some of the inputs from their work such as explosives, water consumption, and selenium dioxide usage are not included in our LCI. The water consumption is not included because as shown in Figure 2, the water is used for washing and not embodied in the product and is therefore considered as water withdrawal and not consumption. GREET does not have input for the usage of explosives. However, previous work has shown that considering the amount of explosives to the final product, impacts associated with the use of explosives for blasting of rocks during the mining stage are negligible.

The crude oil entry from their work was modeled as the use of diesel in non-road engines. This is because of the use of loaders and jiggers during the beneficiation process to produce ore concentrates. Because China currently dominates the production of EMM, the model developed here assumes a production in China. The China electricity grid mix was utilized for the electricity usage.

Table 2. LCI for Electrolytic Manganese Metal production

Material inputs (ton/ton product)	
Manganese content in ore, %	19.26
Manganese carbonate ore	7.81
Manganese in ore	1.50
H_2SO_4,	0.8
Ammonia	0.06
$CaCO_3$	0.01
Energy consumption (mmBtu/ton product)	
Electricity	22.86
Coal	17.05
Diesel	0.02

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