

Updates for Battery Recycling and Materials in GREET® 2019

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ACRONYMS

BOM	bill-of-material
EV	electric vehicle
LCI	life cycle inventory
LIB	lithium-ion battery
NIST	National Institute of Standards and Technology
NMC111	$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$
NMP	N-Methyl-2-Pyrrolidone
TCEQ	Texas Commission on Environmental Quality
USGS	United States Geological Survey

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This memo documents updates in GREET[®] 2019 for (1) four pathways to recycle lithium-ion batteries (LIBs) at the cell level, including a pyrometallurgical recycling pathway, a hydrometallurgical recycling pathway based on inorganic leaching, a hydrometallurgical recycling pathway based on organic leaching, and a direct recycling pathway; (2) material requirements for the production of battery-grade nickel sulfate; (3) life cycle inventory (LCI) for the production of lithium hydroxide; and (4) water consumption for limestone mining.

1 BATTERY RECYCLING

Existing recycling pathways for LIBs in GREET 2018 were based on one pilot-scale process and three lab-scale processes to recycle LiMn_2O_4 batteries (Dunn *et al.* 2014). The unprecedented growth of global electric vehicle (EV) sales in recent years and the foreseeable avalanche of spent EV batteries have garnered increased interest in battery recycling, leading to new developments in recycling technologies and practices. The battery recycling pathways in GREET 2019 are therefore updated to reflect these developments.

In GREET 2019, a new tab is created and dedicated to battery recycling (“Battery Recycling” in GREET2). Batteries to be recycled are assumed to be based on $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111), as it has been the predominant cathode chemistry for EV applications in the past few years. A new hydrometallurgical recycling pathway based on inorganic acid leaching, which has been commercialized in a few countries, notably China, replaces the “intermediate” recycling pathway, which has not gained much traction since its debut. GREET 2019, however, keeps three recycling pathways from GREET 2018: (1) the pyrometallurgical pathway, because it is the other established recycling technology that has been commercialized; (2) the hydrometallurgical pathway based on organic acid leaching, because it remains an active research area in battery recycling technologies; and (3) the direct pathway, because it is one of the focus areas of Argonne’s Advanced Battery Recycling Initiative (Argonne 2019a).

Materials and energy flows associated with the pyrometallurgical, hydrometallurgical with inorganic acid leaching, and direct pathways are taken from Argonne’s EverBatt model (Argonne 2019b), while those associated with the hydrometallurgical with organic acid leaching pathway are derived based on information of the lab-scale process as described in our 2014 report (Dunn *et al.* 2014) and recycling technology-agnostic information (e.g., diesel

consumption for wheel loaders used in the recycling plant) from EverBatt. The LCIs for battery recycling via the four pathways are summarized in Table 1.

Table 1. LCIs for Battery Recycling Pathways (Pyro: Pyrometallurgical; Hydro: Hydrometallurgical)

	Pyro	Hydro: Inorganic Acid Leaching	Hydro: Organic Acid Leaching	Direct
Energy use (mmBtu/ton cells recycled)				
Diesel	0.516	0.516	0.516	0.516
Natural gas	---	2.150	0.837	---
Electricity	4.024	0.107	0.849	2.348
Water use (gal/ton cells recycled)	---	907	---	907
Materials use (ton/ton cells recycled)				
Limestone	0.300	---	---	---
Sand	0.150	---	---	---
Hydrochloric Acid	0.210	0.012	---	---
Hydrogen Peroxide	0.060	0.366	0.065	---
Ammonium Hydroxide	---	0.031	---	---
Sodium Hydroxide	---	0.561	---	---
Sulfuric Acid	0.689	1.078	0.689	---
Soda Ash	---	0.021	0.361	---
Citric Acid	---	---	0.050	---
NMP	---	---	0.000	---
Lithium Carbonate	---	---	---	0.003
Carbon Dioxide	---	---	---	2.200
Non-fuel-combustion process emissions (g/ton cells recycled)				
Carbon Dioxide*	1,103,418	280,334	113,253	199,584

*From combustion of battery materials that contain carbon, thermal decomposition of carbonates, and loss of supercritical CO₂.

Since multiple materials are recovered from the recycling processes, we need to choose a coproduct handling methodology in order to evaluate the environmental impacts for each of the recovered materials. In GREET 2019, we opt for the economic value-based allocation method since it aligns well with the incentives for battery recycling. The allocation factors are calculated based on the amounts of materials recovered and the unit prices of recovered materials, both of which are listed in the Appendix. Users are encouraged to explore the mass-based allocation method by changing the default allocation factors. Users are also encouraged to explore the EverBatt model for coproduct handling methodologies other than allocation (i.e., no allocation and system expansion) and recycling of batteries based on chemistries other than NMC111.

It should be pointed out that in GREET 2019, battery manufacturing is modeled at the pack level, while battery recycling is modeled at the cell level, because information on the end-of-life handling of some of the battery pack components, especially the battery management

system and other electronic parts, is still lacking. Users are encouraged to review the Appendix of our 2018 memo (Dai *et al.* 2018) for the respective bill-of-material (BOM) of NMC111 battery cells and packs, to avoid potential confusion.

2 MATERIALS

2.1 Production of Battery-grade Nickel Sulfate

The LCI for battery-grade nickel sulfate (NiSO_4) production in GREET 2019 is updated. Specifically, in GREET 2019, battery-grade NiSO_4 is assumed to be produced from the reaction of stoichiometric amounts of class 1 nickel and sulfuric acid. Since the reaction is exothermic, no energy requirement is assumed for the process. Details of the update are described in Appendix A of this publication: <https://www.mdpi.com/2313-0105/5/2/48>.

2.2 Production of Lithium Hydroxide

Lithium hydroxide production in previous versions of GREET was modeled based on data from a lithium compounds production facility in Nevada, and it was also assumed that the materials and energy flows for lithium hydroxide production was the same as that for the production of lithium carbonate (Dunn *et al.* 2014). However, information that has become available in recent years suggests that lithium hydroxide is produced commercially by (1) pyrometallurgical and hydrometallurgical refining of Spodumene ore (Albemarle 2018) or (2) reacting lithium carbonate produced from brine with lime (SQM 2019, Jiang *et al.* 2014). The LCI for lithium hydroxide production is therefore updated in GREET 2019 to reflect the industrial practices.

Since at present GREET does not include lithium compounds production from Spodumene ore due to lack of data, this update focuses on lithium hydroxide production from brine. Also, since in 2016 the U.S. imports over 60% of its lithium hydroxide and about 30% of its lithium carbonate from Chile (USGS 2018), in this update, lithium hydroxide is assumed to be produced in Chile from lithium carbonate.

The industrial production of lithium hydroxide starts with reacting lithium carbonate with lime to produce an aqueous solution of lithium hydroxide with a concentration up to 3.5% by weight. Lithium hydroxide monohydrate is subsequently produced from the solution via evaporation, and then dried at 130-140°C and heated to 150-180°C to produce calcined lithium hydroxide (Wietelmann and Steinbild 2014).

In this update, material inputs for lithium hydroxide production are estimated based on stoichiometry, while energy input is estimated based on the theoretical heat requirement for heating the lithium hydroxide solution to 100°C, and then further heating the lithium hydroxide crystal to 180°C. Heat capacity of lithium hydroxide as a function of temperature is taken from the NIST Chemistry WebBook (NIST 2019). Heat of evaporation of water in the solution, however, is not accounted for in the energy input, as the evaporation step can be done in solar evaporation ponds (SQM 2019). The furnace for heating is assumed to be fueled by natural gas, with an efficiency of 80%. Finally, water requirement includes the amount of water consumed in

the causticization reaction, as well as that lost via evaporation. The updated LCI is summarized in Table 2.

Table 2. Updated LCI for LiOH Production

	Quantity	Unit
Energy use		
Total energy	9.696	mmBtu/ton LiOH
Natural gas	9.696	mmBtu/ton LiOH
Water use	6,698	gal/ton LiOH
Material use		
Lithium Carbonate (Li ₂ CO ₃)	1.542	ton/ton LiOH
Lime (CaO)	1.167	ton/ton LiOH

It should be noted that since this LCI is based on engineering calculations, it can be associated with considerable uncertainty. For now, it serves as a placeholder in GREET 2019, and we expect to update lithium compounds production with industry data in GREET 2020.

2.3 Water Consumption for Limestone Mining

The water consumption for limestone mining has been updated in GREET 2019. In previous versions of GREET, water consumption for limestone mining was based on an LCI for limestone quarrying and processing compiled by the University of Tennessee (Lampert *et al.* 2015). The inventory represented the operations of 15 U.S. stone quarries and processing facilities in 2007, and the water consumption was estimated to be 20,000 gal/ton (83L/kg) limestone produced (University of Tennessee 2008).

The inventory, especially the water consumption data, needed to be updated for three reasons. First, limestone producers have become increasingly aware of the water footprint of their practices, and major limestone producers in the U.S. today have adopted various measures (e.g., capturing stormwater runoff for use in the production process, installing water recycling systems) to reduce their water consumptions (Vulcan Materials Company 2019, Martin Marietta 2019, CRH Materials 2019, Lafarge Holcim 2019, CEMEX 2019). Second, the inventory accounted for water consumption for limestone quarrying and processing. Limestone processing included primary cutting and shaping, polishing and honing, secondary shaping, packaging, and storage (University of Tennessee 2008). Some of the processing steps, however, do not apply to limestone in GREET, which is used for lime production, as fluxes for smelting, or as clinker precursor and aggregates for concrete production. Third, the 2008 study did not disclose how the water consumption data were collected and calculated, nor did it disclose what the water consumption consisted of, except that cooling water is needed to operate circular blade saws and diamond wire saws for cutting and shaping (University of Tennessee 2008). Since cooling water is normally discharged with minimal loss, it is possible that the reported 20,000 gal/ton was in fact water withdrawal, not water consumption.

Limestone mining is water intensive. For open-cut mines, if the excavated depth is below the water table, water needs to be pumped out of the pit (a.k.a. dewater) before mining starts, which can result in significant amount of water use (Green *et al.* 2005, Iwanoff 1998). Mine operation also needs water, for mineral processing, saw lubrication, dust control, wastewater treatment, etc. (TCEQ 2012). Most of these water uses, however, are not water consumptions, but water withdrawals, the majority of which will be returned to waterbodies eventually. In GREET, water consumption includes the amount of water that becomes embodied in the products, and the amount of water lost, usually via evaporation, during the production processes. Therefore, water consumption for limestone mining primarily arises from water lost from (1) stone washing (i.e., water trapped on the surface and in the pores of the stones and later lost via evaporation); (2) sedimentation pond to remove fine particles from process water; and (3) storm water retention pond to control increased run-off due to mine operation (TCEQ 2012). Among the three sources, water loss from stone washing is the most significant, and for limestone is estimated as 6% of the bulk volume of the material washed (TCEQ 2012). Assuming a bulk density of 1,300 kg/m³ for limestone (Oates 2000), the water loss from washing is estimated to be 11.06 gal/ton.

In addition to empirical values, we also looked up industry data for this update. Out of the top 10 producers of limestone in the U.S., 3 included water use data in their sustainability reports (CEMEX 2019, Lafarge Holcim 2019, CRH Materials 2019a). The specific water consumption for limestone mining derived from the three reports are summarized in Table 3.

Table 3. 2018 Specific Water Consumption for Limestone Mining for Select Companies

	CEMEX ^a	Lafarge Holcim ^b	CRH Materials ^{c, d}
Water consumption (gal/ton material produced)	24.45	50.19	86.44
Note	Assumed to be the same as the reported specific water consumption for aggregate production.	Allocating all water consumption for their non-cementitious materials production to aggregates production.	Allocating all water consumption for their global materials production to North American aggregates production.

- a. CEMEX 2019
- b. Lafarge Holcim 2019
- c. CRH Materials 2019a
- d. CRH Materials 2019b

The empirical value and the industry data are in relatively good agreement. Considering that the empirical value only represents the water loss from stone washing, and that the specific water consumption derived for Lafarge Holcim and CRH Materials as described above are likely to be overestimates, the specific water consumption reported by CEMEX (that is, 24.45 gal/ton) is selected to update the water consumption for U.S. limestone mining in GREET 2019. Since the value reported by CEMEX represents their global operations, it is also used to update Chilean and Brazilian limestone production in GREET 2019.

APPENDIX: AMOUNTS AND UNIT PRICES OF RECOVERED MATERIALS VIA BATTERY RECYCLING

Table 4. Amounts and Unit Prices of Materials Recovered via Different Recycling Pathways

Materials	Amounts recovered (ton/ton cells recycled)				Unit prices (\$/kg) ^a
	Pyro ^a	Hydro: inorganic acid leaching ^a	Hydro: organic acid leaching ^b	Direct ^a	
CoSO ₄	0.182	0.182	0.182 ^c	---	\$ 19.51
NiSO ₄	0.182	0.182	0.182 ^c	---	\$ 4.29
Li ₂ CO ₃	---	---	0.131	---	\$ 7.90
NMC111	---	---	---	0.312	\$ 20.00
Cu	0.142	0.142	0.142	0.142	\$ 6.60
Al	---	0.074	0.074	0.074	\$ 1.30
MnSO ₄	---	0.177	0.177 ^c	---	\$ 1.13
Graphite	---	0.174	0.174	0.174	\$ 0.28
Electrolyte organics	---	---	---	0.062	\$ 0.15

a. Based on EverBatt.

b. Based on BOM of NMC111 cells reported in Dai *et al.* 2018 and recovered efficiencies reported in Dunn *et al.* 2014.

c. Originally recovered as citrates. Converted into sulfates for downstream production of cathode precursors.

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