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Life-Cycle Inventory of Critical Materials: Nickel, Copper, Titanium, and Rare-Earth Elements

Energy Systems and Infrastructure Analysis Division

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by

Rakesh Krishnamoorthy Iyer and Jarod C. Kelly Energy Systems and Infrastructure Analysis Division, Argonne National Laboratory

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ACRONYMS

Ag	silver
As	arsenic
Au	gold
C_2H2O_4	oxalic acid
$CaTiO_3$	perovskite
CIGS	copper-indium-gallium-selenide
CIS	copper-indium-selenide
Cl	chlorine
Class I Ni	metal
Co	cobalt
CO_2	carbon dioxide
Cr	chromium
Cu	copper
$CuFeS_2$	chalcopyrite
EPA	2-ethyl 3-propyl acrolein
EVs	electric vehicles
Fe	iron
FeTiO ₃	ilmenite
GREET®	Greenhouse gases, Regulated Emissions, and Energy use in Transportation
HF	hydrogen fluoride
HFTO	Hydrogen Fuel Cell Technologies Office
$\begin{array}{l} H_2O\\ H_2O_2\\ H_2O_5\\ H_2SO_4 \end{array}$	water hydrogen peroxide hydrogen pentoxide sulfuric acid
LCA	life-cycle analysis
LCI	life-cycle inventory
LIBs	lithium-ion batteries
LiF	lithium fluoride
m ³	actual volume
Mg	magnesium
MgCl ₂	magnesium chloride
MgO	magnesia
MSE	molten salt electrolysis

NH ₃ NH ₄ HCO ₃ (NH ₄) ₂ SO ₄ Ni (Ni,Fe) ₉ S ₈ Ni-MH NiO NiSO ₄ Nm ³	ammonia ammonium bicarbonate ammonium sulfate nickel pentlandite nickel-metal hydride nickel oxide nickel sulfate normal volume
O ₂	oxygen
O ₃	ozone
P2O4	Di-2-ethylhexyl phosphoric acid
P5O7	2-ethylhexyl phosphoric acid mono-2-ethylhexylester
Pb	lead
PCl ₃	phosphorus trichloride
Pt	platinum
RECls	rare-earth chlorides
REEs	rare-earth elements
REFs	rare-earth fluorides
REOs	rare-earth oxides
Sb	antimony
Se	selenium
Si	silicon
SiO ₂	silica
SO_2	sulfur dioxide
SS	sodium silicate
Те	tellurium
Ti	titanium
TiCl ₄	titanium chloride; titanium tetrachloride
TiO ₂	titanium dioxide
USGS	United States Geological Survey
VTO	Vehicle Technologies Office (VTO)
YSZ	yttria-stabilized zirconia
Zn	zinc

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ABSTRACT

The United States has developed a list of critical minerals/materials whose sustained and reliable supply is pivotal to the robust functioning of critical industrial sectors. A key concern with these minerals is their environmental effects as a function of their production location. This requires material and energy flow details for their processing steps. This report provides a life-cycle inventory (LCI) for producing four critical minerals and/or material systems (nickel, copper, titanium, and rare-earth elements) incorporated in the updated GREET[®] (Greenhouse gases, Regulated Emissions, and Energy use in Technologies) model. For these systems, we provide an LCI as a function of production location – domestic (within the United States) and international (geographies from where the US imports these minerals). Our LCI also considers variations in ore grades for nickel and copper. This report also provides an LCI for all intermediate materials used to produce these critical materials.

1 INTRODUCTION

In 2022, the United States declared a final list of 50 critical minerals whose sustained and reliable supply is essential to the nation's economic prosperity and security (US Department of the Interior, 2022; US DoE, 2011; US DOE, 2020). A key area of focus regarding these materials is to develop alternative, stable sources of supply for these materials, both within and outside the US in favorable geographies (US DOE, 2020). This has also raised questions regarding the environmental impacts of producing these elements in alternative locations, especially compared to their baseline counterparts (Babbitt et al., 2021; US DOE, 2020). This is vital as it helps to: (a) Identify the net environmental effects of switching from existing to newer production locations for critical minerals; and (b) Determine processes/technologies with high contributions to environmental impacts of producing such minerals that must be replaced by other processes/technologies to make their production in alternative locations environmentally favorable over the existing baseline (Babbitt et al., 2021; US DOE, 2020).

This report focuses on four such mineral/material systems that are either critical or important for the United States across several sectors: nickel (Ni), copper (Cu), titanium (Ti), and rare-earth elements (REEs). Three of these materials are considered critical by the US – Ni, Ti, and REEs (US Department of the Interior, 2022) – as they are vital for sectors that are pertinent to various national goals of the US. These sectors include lithium-ion batteries (LIBs) for electric vehicles (EVs), clean energy, defense, electronics, and lighting (Gaustad et al., 2018). Further, copper (Cu) is an essential component of vehicles, especially Evs through their substantial use as current collectors in LIBs. Moreover, the US is substantially dependent on imports of these minerals (> 50% of their overall consumption) (USGS, 2022a). A critical chunk of these imports often come from nations that have less stringent environmental standards (US DOE, 2020; USGS, 2022a), which can cause more significant environmental stress from their production compared to locations with more demanding emission standards (Kelly et al., 2019; Winjobi et al., 2022). Hence, we account for these aspects in the updated GREET model for all four mineral/material systems (Ni, Cu, Ti, and REEs).

The rest of this report is as follows: nickel is covered in Section 2, copper in Section 3, titanium in Section 4, and rare-earth elements in Section 5. We first discuss each of these materials' significance, followed by their current state of production and imports in the US. Next, we provide the material and energy flows (LCI) for their production in the final desired form. We also provide LCIs for producing intermediate materials used in producing any of these four minerals/material systems in Section 6. More details are given in the individual sections.

2 NICKEL (Ni)

2.1 Significance, Production and Imports

Global nickel (Ni) demand has risen substantially over the past few decades, driven by its need for residential, industrial, and commercial applications (Elshkaki et al., 2017). This growth has been propelled by its advantageous properties, such as corrosion resistance in different media, moderate strength, high malleability and ductility, and excellent high-temperature stability (Benavides et al., 2015; Elshkaki et al., 2017; Kerfoot, 2000). Ni is used in many sectors, including construction, infrastructure, petrochemicals, transportation, fabrication, appliances, and industrial machinery (Deng and Gong, 2018; Elshkaki et al., 2017; Guohua et al., 2021; Khoo et al., 2017b). Across these sectors, Ni is used in a variety of forms and/or material systems, such as metal (Class I Ni), stainless steel, superalloys, ferronickel, nickel sulfate (NiSO4), and multi-elemental systems (e.g., cathodes of lithium-ion batteries) (Mudd, 2010). Such vast use of Ni for diverse applications, coupled with its superior properties, the strong outlook for technologies that employ Ni, and the unlikely possibility of its substitution with other metals, has led to its classification as a *critical mineral* by the United States (Elshkaki et al., 2017; Kerfoot, 2000; US Department of the Interior, 2022; US DOE, 2020).

In terms of its occurrence, Ni ranks 24th in elemental availability in the earth's crust (0.008%) – greater than copper (Cu), zinc (Zn), and lead (Pb) (Kerfoot, 2000; Mudd, 2010). However, unlike these elements, Ni suffers from a lack of ore bodies with significant concentration (Kerfoot, 2000). Major economically extractable reserves of Ni can be classified into two groups of ores: sulfide and laterite (oxide) (Kerfoot, 2000; Mudd, 2010; Mudd and Jowitt, 2014). Table 1 shows important characteristics of both these types of Ni ores/minerals (Kerfoot, 2000). Note that while the minerals within these ores contain significant amounts of Ni (Table 1), the actual Ni content in ores is typically less than 3 wt.% (Mudd, 2010; Mudd and Jowitt, 2014). Further, while the bulk share of Ni is present in laterite ores (~80%), the relative lack of Ni concentration (ore grade) in these ores results in the majority of Ni (~60%) being produced from sulfide ores (Kerfoot, 2000; Mudd, 2010; Mudd and Jowitt, 2014). Major Ni-producing minerals include pentlandite (sulfide ore) and nickeliferous limonite and garnierite (oxide ores).

While Ni is produced in various forms from its ores, in this report, we focus solely on Ni in metallic form (Class I Ni). At the mine level, the United States is a minor player in global Ni production, accounting for < 1% share (17,600 metric tons in 2018) of world Ni output, with no data available for domestic Class I Ni production (USGS, 2022b). Also, the US Geological Survey (USGS) data shows that total Class I Ni¹ imports exceed its exports and broadly match the U.S.'s primary Ni consumption (USGS, 2022b). This indicates that the US entirely depends on imports to meet its primary Ni metal demand. Table 2 provides the share (%) of Ni metal produced from domestic and import sources, along with the share of their respective Ni production from sulfide and laterite ores (USGS, 2022b). Note that this refers to the mix of

¹ Based on USGS classification, Class I Ni is assumed to contain all Ni produced in unwrought form (cathodes, pellets, and briquets), powders, and flakes (USGS, 2022b).

Class I Ni imports and not necessarily the mix associated with the original location of Ni ore mining. The two mixes often differ, given the globalized nature of the Ni supply chain, which enables Ni mining in one country and its processing in a different country (Mudd and Jowitt, 2014; USGS, 2022b).

Ores	Mineral	Chemical formula	Ni content (%)
	Pentlandite	(Ni,Fe) ₉ S ₈	34.22
	Millerite	NiS	64.67
Sulfides	Heazlewoodite	Ni ₃ S ₂	73.30
	Polydymite	Ni ₃ S ₄	57.86
	Siegenite	$(Co,Ni)_3S_4$	28.89
	Violarite	Ni ₂ FeS ₄	38.94
Latarita/Silicata	Garnierite	$(Ni,Mg)_6Si_4O_{10}(OH)_8$	≤ 47
Laterne/Sincate	Nickeliferous limonite	(Fe,Ni)O(OH).nH ₂ O	Low
	Niccolite	NiAs	43.92
Others	Rammelsbergite	NiAs ₂	28.15
Oulers	Gersdorffite	NiAsS	35.42
	Breithauptite	NiSb	32.53

 Table 1: Important Characteristics of Nickel Ores (reproduced from (Kerfoot, 2000))

Table 2: Share of Class I Ni import from different nations (based on (USGS, 2022b))

Nation	Share of supply/import in US consumption mix of Class I Ni (%)
Australia	15.63
Brazil	0.10
Canada	44.17
Finland	9.11
Japan	3.09
Norway	11.61
Russia	7.85
China	0.36
South Africa	4.44
Others	3.64

2.2 Nickel Production Processes

A previous Argonne report details the exact nature of Ni production from both sulfide and laterite ores (Benavides et al., 2015). Here, we provide a summary of the processes involved in Ni production from both these ore sources. Figures 1 and 2 present the schematic to produce Ni from sulfide and laterite ores, respectively.



Figure 1: Schematic of Ni production from sulfidic ores



Figure 2: Schematic of Ni production from laterite ores

2.2.1 Nickel Production: Sulfide Ore

Sulfide ores are the dominant source of global Ni production (60% share) due to the better economic feasibility of Ni extraction from these ores compared to laterite ores (Mudd,

2010; Mudd and Jowitt, 2014). Ni production from sulfide ores is described below based on multiple references (Benavides et al., 2015; Elshkaki et al., 2017; Kerfoot, 2000; Mudd, 2010; Mudd and Jowitt, 2014).

Sulfide ore-based Ni production comprises four steps: mining, beneficiation, Ni extraction, and refining (Figure 1). Sulfide ores typically contain three minerals - pentlandite $((Ni,Fe)_9S_8)$, nickeliferous pyrrhotite (Ni-containing Fe₇S₈), and chalcopyrite (CuFeS₂) – in varying proportions (Kerfoot, 2000). Of these minerals, chalcopyrite is leveraged for Cu production, while pyrrhotite has limited Ni content. Hence, it is pentlandite that constitutes almost the entire share of sulfide-based global Ni production (Kerfoot, 2000). The separation of these three minerals is generally a challenge at the mine level, mainly for economic reasons, so it is only pursued when mandated by environmental regulations (such as in Canada) (Kerfoot, 2000). Instead, the typical approach is to separate the concerned elements post-mining, either at beneficiation, or during primary Ni extraction.

As shown in Figure 1, the mined ore is first concentrated using a physical treatment method (such as comminution) and then subjected to froth flotation and/or magnetic separation to obtain Ni-rich concentrate (Ni-content: 5-15 wt.%). Flotation aids the removal of both chalcopyrite and pyrrhotite from ore (to leave behind pentlandite), while magnetic separation eases the separation of pyrrhotite (Kerfoot, 2000). Ni concentrate is treated in primary Ni extraction processes (or pyrometallurgical processing) to produce Ni-rich matte (Ni-content: 60-80 wt.%). Pyrometallurgy involves three operations conducted in series: (a) Roasting, where the sulfur content in Ni-concentrate is driven off as sulfur dioxide (SO₂) by heating the concentrate at high temperatures (600-700°C) in air (excess oxygen); (b) Smelting, where the roasted product is melted together with silica (SiO₂) to produce two immiscible phases: molten sulfide solution (used subsequently) and ferrosilicate slag (that separates iron from copper; slag is discarded); and (c) Converting, where both roasting and smelting-related steps are repeated to remove more sulfur (as SO₂) and iron (as slag). The general practice is to conduct all three pyrometallurgical operations in a single unit. The output *matte* contains both Ni and other valuable elements like copper (Cu) and noble metals (such as tellurium (Te), selenium (Se), and platinum group metals like gold (Au) and platinum (Pt)). Hence, matte is processed further to separate these elements (usually via hydrometallurgy) and produce them for commercial applications.

The last step is refining, which can be conducted via electrorefining, electrowinning, or the most commonly used carbonyl refining. Carbonyl refining is conducted in two steps: (a) Reaction of Ni *matte* with high-pressure carbon monoxide (CO) at 40-80°C to produce nickel tetracarbonyl (Ni(CO)₄); and (b) Decomposition of Ni(CO)₄ at 150-300°C to Ni and CO. Carbonyl refining is favored over other refining processes as it facilitates the separation of other metals from Ni *matte* as carbonyls that decompose at different temperatures, and that can be used to obtain the desired metal of high purity level.

2.2.2 Nickel Production: Laterite Ore

Laterite (oxide) ores are formed through periodic weathering of peridotite rocks containing olivine (magnesium-iron silicate with up to 0.3 wt.% Ni) and serpentine (hydrated

magnesium silicate that contains Ni) (Kerfoot, 2000). Weathering due to groundwater causes Ni, SiO₂, and magnesium (Mg) to dissolve in it and leach to lower depths in laterite deposits as an acidic solution. This solution neutralizes upon reaction with rock/soil to form hydrated silicates of Ni and Mg, creating in turn two distinct zones of Ni presence: nickeliferous limonite zone, and silicate or *garnierite* zone (Kerfoot, 2000). Limonite contains both iron (Fe) and Ni as oxides in a solid solution, along with cobalt (Co) and chromium (Cr), while being depleted of SiO₂ and Mg content. Conversely, Fe and Ni are fully separated in the garnierite zone, with Ni present in silicate minerals with high magnesia (MgO) content.

Figure 2 shows the schematic of laterite ore production, while a brief description of this process is given here, based on multiple sources (Benavides et al., 2015; Elshkaki et al., 2017; Kerfoot, 2000; Mudd, 2010; Mudd and Jowitt, 2014). Laterite ores are selectively mined and screened to separate into limonite and garnierite fractions (if one fraction is dominant, only that is used to produce Ni). Unlike sulfide ores, laterite ores cannot be treated using standard beneficiation methods due to the combined presence of Fe and Ni in solid solution (for the limonite fraction) and the strong bonding of Ni and Fe with oxygen (for both limonite and garnierite fractions). The ores are first dried and heated to reduce their moisture content (up to 45%) down to 15-20%, and then calcined further to reduce the ores and bring down the moisture to acceptable levels. The obtained *residue* at the end of this step (the equivalent of Ni concentrate in sulfide-based extraction) is subsequently used to extract primary Ni.

Different processing techniques are used to extract Ni from the *residue* obtained via limonite and garnierite fractions due to differences in their respective chemical composition. Limonites exhibit homogeneity in their material composition and mineralogy, rendering them suitable for hydrometallurgical processing. In contrast, silicate minerals typically show mineralogical and chemical heterogeneity, so they are treated via pyrometallurgical methods that provide flexibility in processing.

In the case of laterite (limonite) ores, hydrometallurgy is used not only due to their homogeneity (both chemical and mineral) but also because of the presence of other valuable byproducts, such as Co and Cr. Hydrometallurgy involves the leaching of residue or matte in a sulfate or chloride solution to dissolve Ni and other elements and produce nickel sulfate or chloride, which is electro-refined or reacted with hydrogen (H₂) to produce Class I Ni cathode. Prominent hydrometallurgical techniques include ammonia pressure leaching (leaching agent or LA: ammonia), atmospheric acid leaching (LA: acidic sulfate solution in ambient atmosphere), acid pressure leaching (LA: sulfuric acid), and chloride leaching (LA: chloride solution). Acid pressure leaching is considered the most optimal of all methods due to the high purity level of final products obtained. However, this method cannot be used for ores that contain substantial amounts of acid-consuming minerals, such as garnierite ores due to their high magnesia content. Hydrometallurgy can also be combined with roasting to enhance its effectiveness, as in the Caron process where calcined Ni concentrate is obtained by roasting laterite ores, leaching the residue in ammoniacal carbonate solution, and then boiled to obtain Ni as concentrate precipitate. This precipitate can be refined further to produce nickel oxide (NiO), and subsequently, Ni powder.

For laterite (garnierite) ores, the nature of pyrometallurgical treatment is different from that used for sulfide ores due to the combined presence of Fe and Ni, as well as of magnesia and SiO₂. Here, pyrometallurgical processing involves adding coal and molten elemental sulfur to Ni material (either ferronickel, calcined Ni, or *Ni-concentrate*) in the smelter. Coal (carbon) reduces the initial nickel and ferric oxides to their respective metallic forms, after which these metals react with sulfur to form their respective sulfides. Subsequent smelting (high-temperature heating in air) enables the sulfur to be released as SO₂, leaving behind Ni that can be purified via carbonyl refining to produce Class I Ni (described in the previous subsection). Fe is removed with SiO₂ (present in ores) as ferrosilicate slag, along with Mg. While the exothermic nature of SO₂ evolution provides some energy for smelting, laterite ores typically consume 2-3 times the energy needed to process sulfide ores via pyrometallurgical processing (Kerfoot, 2000). Note that pyrometallurgical treatment of laterite ores is also used to produce ferronickel, but we do not dwell on that aspect here as our focus is restricted solely to Class I Ni production.

2.3 Material and Energy Flows for Nickel Production

2.3.1 Context of Update

The rise in global Ni demand has caused a decline in its ore concentration (or ore grade) over time (Elshkaki et al., 2017; Mudd, 2010; Norgate and Haque, 2010; Norgate and Jahanshahi, 2010). This is expected to increase further in future with the likely increase in demand across several sectors, including those related to clean energy (e.g., rechargeable batteries) (Mudd, 2010; Mudd and Jowitt, 2014). For every kilogram of nickel produced, the decline in ore grade will increase the material and energy requirements for its production (Norgate and Haque, 2010; Norgate and Jahanshahi, 2010; Wei et al., 2020). The reduced presence of Ni in sulfide ores has also caused a shift towards Ni production from laterite ores, which currently contribute ~40% of global Ni demand (Mudd, 2010; Mudd and Jowitt, 2014). However, the specific nature of processes needed to produce Ni from laterite ores results in higher energy intensity of production from these ores over their sulfidic counterpart (Kerfoot, 2000; Mudd, 2010; Mudd and Jowitt, 2014). Further, the US sources Ni from multiple nations due to its lack of domestic reserves (USGS, 2022b). The location of Ni production and processing has a significant bearing on the electricity used during its processing (i.e., electric grid mix), and thereby, on the associated impacts of Ni production. Thus, all three aforementioned factors - ore grade, type, and location - together influence the environmental profile of Ni production, and therefore, should all be considered for a holistic analysis of the environmental impacts of producing this metal.

In GREET 2021 (Wang et al., 2021), we considered the inventory for Ni production as reported by the Nickel Institute (Sphera, 2020). This source provides a single inventory across all three factors (ore grade, location, and type) for all Ni mines and processing facilities, except those in China. Hence, it is difficult to segregate the effect of individual factors on the environmental impacts of Ni production. In GREET 2022 (Wang et al., 2022), to address this concern, we provide the life-cycle inventory (LCI) of Class I Ni consumed in the US as a

function of these three factors. In the subsequent subsections, we describe the approach used to develop LCI for both sulfide and laterite ores in GREET 2022.

2.3.2 Approach: Sulfide Ores

For sulfide ores, an LCI is provided for Ni production as a function of three factors: (a) Ore grade (wt.% Ni content in ore); (b) Location of Ni ore mining and beneficiation; and (c) Location of Ni processing facility (primary Ni extraction and refining).

With reference to ore grade, literature shows that variation in this parameter influences the material and energy needs for only the mining and beneficiation stages, without affecting the other processes (primary Ni extraction and refining) (Norgate and Haque, 2010; Norgate and Jahanshahi, 2011; Wei et al., 2020). This is due to the consistent Ni content (5-15 wt.%) of Ni concentrate produced at the end of beneficiation. Among the papers surveyed in our literature review, Wei et al. (2020) provide the most recent LCI for Ni production in Australia, based on a 2.05% Ni ore grade. This study also reports the variation in life-cycle energy needs for Ni production from sulfide ores as a function of ore grade, both for total Ni production and for the individual stages (mining and beneficiation are combined as a single stage). Hence, we used data from Wei et al. (2020), along with several assumptions and caveats, to understand the effect of ore grade on mining and beneficiation-related material and energy requirements. The relevant variables used (along with their description) are given in Table 3, while the associated equations with this description are provided below.

Variables	Description	
Ni - S	For nickel production from sulfide ores	
$OG_{Default,Ni-S}$	Default ore grade, obtained from (Wei et al., 2020)	
PE _{Mining,Default,Ni-S}	Process energy data for mining of the default ore grade, obtained from (Wei et al., 2020)	
PE _{Benef} iciation,Default,Ni-S	Process energy data for beneficiation of the default ore grade, obtained from (Wei et al., 2020)	
LCE _{Mining,Default,Ni-S}	Life-cycle energy consumed for the mining stage for the default ore grade, calculated using process-related data from (Wei et al., 2020) in GREET2	
LCE _{Benef} iciation,Default,Ni–S	Life-cycle energy consumed only for beneficiation stage for the default ore grade, calculated using process-related data from (Wei et al., 2020) in GREET2 (ignores all life-cycle energy consumed in prior stages, i.e., mining stage)	
$LCE_{M+B,Default,Ni-S}$	Life-cycle energy consumed till the beneficiation stage (sum of mining and beneficiation stages) for the default ore grade, calculated using data from (Wei et al., 2020) in GREET2	
$S_{mining,Ni-S}$	Share (%) of mining in life-cycle energy consumed till beneficiation	
$S_{beneficiation,Ni-S}$	Share (%) of beneficiation in life-cycle energy consumed till beneficiation	

 Table 3: Description of variables used for sulfide ore-related analysis

Table 3 (Cont.)

Variables	Description	
$PE_{M+B,Default,Ni-S}$	Process energy across both the mining and beneficiation stages for the default ore grade	
Ratio _{LCE-to-PE,Ni-S}	Ratio of life-cycle energy to primary energy across both the mining and beneficiation stages (calculated using the default ore grade, but applies to all ore grades)	
$PE_{Mining-Diesel,share,Ni-S}$	Life-cycle energy for the mining stage from diesel	
$PE_{Mining-Electricity,share,Ni-S}$	Life-cycle energy for the mining stage from electricity	
$LCE_{M+B,OG,Ni-S}$	Life-cycle energy consumed till the beneficiation stage (sum of mining and beneficiation stages) for ore grade (OG)	
OG(Ni-S)	Ore grade (0.5%, 1%, 1.5%, 2%, 2.5%, and 3%)	
$PE_{M+B,OG,Ni-S}$	Total process energy consumed for the mining and beneficiation steps for different ore grades (OG)	
PE _{Mining,OG,Ni-S}	Process energy consumed for mining $(PE_{Mining,OG})$ for difference ore grades (OG)	
PE _{Benef} iciation,OG,Ni-S	Process energy consumed for beneficiation ($PE_{Beneficiation,OG}$) for different ore grades (OG)	
PE _{Mining-Diesel,OG,Ni-S}	Mining-related process energy using diesel for different ore grades (OG)	
PE _{Mining-Electricity,OG,Ni-S}	Mining-related process energy using electricity for different ore grades (OG)	
LCE _{laterite-Ni,pyro}	Life-cycle embodied energy of processing Ni from laterite ores using pyrometallurgical processing	
LCE _{laterite-Ni,hydro}	Life-cycle embodied energy of processing Ni from laterite ores using hydrometallurgical processing	

First, we consider the 2.05% Ni ore grade from Wei et al. (2020) as the default ore grade in GREET 2022 ($OG_{Default,Ni-S} = 2.05\%$). This is because the ore grade in Wei et al. (2020) is within the typical range of ore grades for economically extractable sulfidic Ni ore (1.5-3.0%) (Mudd, 2010; Mudd and Jowitt, 2014). Next, we used the process energy data from Wei et al. (2020) for mining and beneficiation ($PE_{Mining,Default,Ni-S}$ and $PE_{Beneficiation,Default,Ni-S}$, respectively) of the default ore grade in GREET2 to calculate:

- a) Total life-cycle energy of the mining $(LCE_{Mining,Default,Ni-S})$ and beneficiation $(LCE_{Beneficiation,Default,Ni-S})$ stages and their total sum $(LCE_{M+B,Default,Ni-S})$, obtained using Equation 1);
- b) Individual share (%) of contributions from each stage in the total life-cycle energy across both stages, obtained using Equations 2 and 3 for mining ($S_{mining,Ni-S} = 51.72\%$) and beneficiation ($S_{beneficiation,Ni-S} = 48.28\%$) respectively; and
- c) The ratio of life-cycle energy to primary energy across both stages combined (computed using Equation 4; $Ratio_{LCE-to-PE,Ni-S} = 1.99$).

Hence, using the LCI from Wei et al. (2020) for the default ore grade in GREET2, we computed the share of diesel ($PE_{Mining-Diesel,share,Ni-S} = 30.4\%$) and electricity ($PE_{Mining-Electricity,share,Ni-S} = 69.6\%$) in process energy consumed till the mining stage ($PE_{Mining,Default,Ni-S}$). Note that all these values/parameters are calculated for the default ore grade (2.05%), and that all the energy used for the beneficiation process is electricity.

$$LCE_{M+B,Default,Ni-S} = LCE_{Mining,Default,Ni-S} + LCE_{Beneficiation,Default,Ni-S}$$
(1)

$$S_{mining,Ni-S} = \frac{LCE_{Mining,Default,Ni-S}}{LCE_{M+B,Default,Ni-S}}$$
(2)

$$S_{beneficiation,Ni-S} = \frac{LCE_{Beneficiation,Default,Ni-S}}{LCE_{M+B,Default,Ni-S}}$$
(3)

$$Ratio_{LCE-to-PE,Ni-S} = \frac{PE_{M+B,Default,Ni-S}}{LCE_{M+B,Default,Ni-S}}$$
(4)

To consider the variation in mining and beneficiation-related energy needs for different ore grades, we assume that three sets of above-mentioned parameters are constant across all ore grades. These are:

- a) Conversion factor for life-cycle energy to primary energy (i.e., *Ratio_{LCE-to-PE,Ni-S}* = 1.99);
- b) Individual contributions (%) of mining ($S_{Mining,Ni-S} = 51.72\%$) and beneficiation ($S_{Beneficiation,Ni-S} = 48.28\%$) stages to the total life-cycle and process energy needs spanning both stages;
- c) The share of diesel ($LCE_{Mining-Diesel,Ni-S} = 30.4\%$) and electricity ($LCE_{Mining-Electricity,Ni-S} = 69.6\%$) in life-cycle, and thereby, process energy of mining stage.

We also plotted the results reported by Wei et al. (2020) for the variation in life-cycle energy till the beneficiation stage as a function of Ni ore grade and obtained the corresponding equation to represent this variation (Equation 5). Here, $LCE_{M+B,OG,Ni-S}$ is the life-cycle energy consumed across the mining and beneficiation stages as a function of ore grade (*OG*).

We consider six additional ore grades for analysis in GREET2 (0.5%, 1%, 1.5%, 2%, 2.5%, and 3%). To compute the fuel-wise process energy needed for the mining and beneficiation steps for these ore grades, we employ a four-step process, considering the three assumptions on parameters' constancy. First, we use Equation 5 to obtain the life-cycle energy consumed for the mining and beneficiation steps combined ($LCE_{M+B,OG,Ni-S}$) for different ore grades (OG (Ni - S). Next, we employ Equation 6 to obtain the total process energy consumed for the mining and beneficiation steps for each ore grade ($PE_{M+B,OG,Ni-S}$). In the third step, we use Equations 7 and 8 to obtain the process energy used separately for the mining ($PE_{Mining,OG,Ni-S}$) and beneficiation ($PE_{Beneficiation,OG,Ni-S}$) stages for different ore grades.

Finally, we use Equations 9 and 10 to split the process energy used for mining into diesel $(PE_{Mining-Diesel,OG,Ni-S})$ and electricity $(PE_{Mining-Electricity,OG,Ni-S})$ for each ore grade. All the energy used for beneficiation is electrical energy, so splitting is unnecessary.

$$LCE_{M+B,OG,Ni-S} = 106.71 \times OG \ (Ni-S)^{-1.032}$$
(5)

$$PE_{M+B,OG,Ni-S} = \frac{LCE_{M+B,OG,Ni-S}}{Ratio_{LCE-to-PE,Ni-S}}$$
(6)

$$PE_{Mining,OG,Ni-S} = S_{mining,Ni-S} \times PE_{M+B,OG,Ni-S}$$
(7)

$$PE_{Beneficiation,OG,Ni-S} = S_{beneficiation,Ni-S} \times PE_{M+B,OG,Ni-S}$$
(8)

$$PE_{Mining-Diesel,OG,Ni-S} = PE_{Mining-Diesel,share,Ni-S} \times PE_{Mining,OG,Ni-S}$$
(9)

$$PE_{Mining-Electricity,OG,Ni-S} = PE_{Mining-Electricity,share,Ni-S} \times PE_{Mining,OG,Ni-S}$$
(10)

Wei et al. (2020) do not report any material use for Ni production's mining or beneficiation stages. Hence, we use the same material-related inventory for these stages as already provided in GREET 2021 (Wang et al., 2021). However, to avoid double counting, we do not consider the life-cycle energy use associated with these materials (e.g., ammonium nitrate used for mining) in the process energy consumption calculation procedure for mining and beneficiation steps as a function of ore grade. Thus, while we *do* account for the variation in energy needs of Ni production with changes in ore grade, we are unable to account for such variation in material requirements due to lack of suitable data. Table 4 provides the variation in energy inputs for mining and beneficiation steps used for sulfide ores for the different ore grades considered in GREET2 (Wang et al., 2022). Note that for the default ore grade, material inputs consumed during mining and beneficiation stages account for < 10% of its total productionrelated environmental impacts for all ore grades. This suggests that even if material inputs were to vary with ore grade for these two stages, this might not significantly affect the environmental burdens of Ni production from sulfide ores.

Post-beneficiation, the LCI for Ni production from sulfide ores is independent of the initial ore grade (Norgate and Haque, 2010; Norgate and Jahanshahi, 2011; Wei et al., 2020). Hence, we use the inventory from Wei et al. (2020) to account for the primary Ni extraction (pyrometallurgy) and refining stages. Material inputs for these stages are not provided in Wei et al. (2020); hence, we use the exact input quantities from GREET 2021 in GREET 2022. While the use of these materials is confirmed by Wei et al. (2020), the quantities of most materials are not provided. However, for some materials such as ammonia, Wei et al. (2020) provide the quantity used, which is reflected in GREET2022. Tables 4-6 provide the detailed LCI (material and energy flows) for all steps of Ni production.

One grade $(9/)$	Energy inputs (mmBtu/ton)		
Ore grade (76)	Mining	Beneficiation	
0.50%	48.837	45.589	
1.00%	23.883	22.295	
1.50%	15.716	14.671	
2.00%	11.679	10.903	
2.05% (Default)	10.152	9.477	
2.50%	9.277	8.660	
3.00%	7.686	7.175	
Break-up: For all ore grades	Diesel: 30.4%; Electricity: 69.6%	Electricity: 100%	

Table 4: Energy inputs as a function of ore grade for Ni production from sulfide ores

Table 5: Material flows for Ni production from sulfide ores

Matarial Innuts (tan/tan Ni)	Ni Production Stages			
Material inputs (ton/ton Ni)	Mining	Beneficiation	Primary Extraction	Refining
Ammonium nitrate	0.092			
Steel		0.087		
Lime		0.096	0.128	0.021
Limestone			1.745	
Sulfur			0.611	
Coke			0.316	
Sodium hydroxide			0.007	0.111
Sand			2.529	0.001
Ammonia			0.001	0.637
Oxygen			3.093	0.333
Sulfuric acid		0.002	0.698	0.159
Soda ash		0.021	0.004	0.190
Hydrogen				0.07

Table 6: Energy flows for Ni production from sulfide ores

Enorgy Inputs	Ni Production Stages			
(mmBtu/ton Ni)	Mining (Default ore grade)	Beneficiation	Primary Extraction	Refining
Diesel	3.090		5.299	
Natural gas			6.648	14.999
Coal			9.238	
Electricity	7.062	9.477	2.149	8.969

Apart from ore grade, ore source (location) plays a vital role in influencing the emissions impacts of Ni production. Given the globalized nature of Ni production, where ore mining and its subsequent processing may occur at different locations, we consider two electric grid mixes to account for these differences in GREET 2022: one for mining and beneficiation, and another for primary Ni extraction and refining. The grid mix for mining and beneficiation is derived based

on the share (%) of mine-level Ni production of different nations in the US Class I Ni supply (including domestic and imports) grid mix for primary Ni extraction (pyrometallurgical processing) and refining is based on the share (%) of different nations in Class I Ni imports by the United States. Table 7 provides both these grid mixes.

Countries	Share in production (%)		
Countries	Nickel ore Production	Ni extraction and refining	
Australia	20.45	15.63	
Brazil	0.00	0.10	
Canada	21.11	44.17	
Finland	5.23	9.11	
Japan	0.00	3.09	
New Caledonia	0.00	0.00	
Norway	0.03	11.61	
Russia	32.67	7.85	
China	13.21	0.36	
Indonesia	0.00	0.00	
Philippines	0.00	0.00	
South Africa	5.19	4.44	
Others	2.11	3.64	

Table 7: Grid mixes used for Ni production processes from sulfide ores

An important caveat here is the lack of process emissions for any of the Ni production steps in GREET 2022, which is a major difference when compared with GREET 2021. This requires a detailed explanation, which is given below in succinct detail for the users.

GREET 2021 (Wang et al., 2021) obtains data for process emissions from the data reported by the Nickel Institute (Sphera, 2020). However, these emissions are based on combined Ni production from sulfide and laterite ores, even when a particular gas's actual emissions often depend on the ore used. One critical gaseous emission is SO₂, which is emitted during Ni production from sulfidic ores, mainly during pyrometallurgical processing (roasting) where sulfur is removed via oxidation (Kerfoot, 2000). However, since the Nickel Institute report does not provide a clear breakdown of the share (%) of Ni production from sulfide and laterite ores, it is not possible to use their data to compute the SO₂ emissions from sulfide ores. Hence, we could not use the data from the previous GREET versions in this analysis, as our focus is to segregate the LCI and resultant impacts of Ni production from sulfidic and laterite ores.

In contrast to the Nickel Institute report (Sphera, 2020), Wei et al. (2020) – the source used for the LCI in GREET 2022 – does not provide any data on process emissions. With regard to SO₂, Wei et al. (2020) assume that SO₂ is captured in a concentrated form from flue gas produced during flash smelting and converting, and then used to produce sulfuric acid (H₂SO₄). Given the absence of further data, we assume that this conversion process is 100% efficient, i.e., all the SO₂ gets converted to H₂SO₄, meaning that no SO₂ is emitted during this process. We acknowledge that this assumption may underestimate total SO₂ emissions, even after accounting for efforts to lower SO_2 emissions during Ni production in recent years via use of desulfurization technologies. However, considering the lack of other data, and to be consistent with the reference used for this analysis, we have not provided any process emissions for Ni production in GREET 2022.

An alternative way to account for SO_2 emissions in particular can be to use the data on air and oxygen amounts provided by Wei et al. (2020) to estimate the actual SO_2 emissions during pyrometallurgical processing. We consider four assumptions for calculating SO_2 emissions:

- a) 1:1 conversion between the normal volume (Nm³) and actual volume (m³) for air and oxygen (O₂) used in the flash smelting and converting stages;
- b) O₂ content of 21% in air;
- c) Density of air and O_2 as 1.274 and 1.408 kg/m³, respectively (Evans, 2015) and
- d) 80% efficiency of O_2 use, i.e., only 80% of O_2 in both air and O_2 reacts with sulfur from ore to form SO_2 .

Based on these assumptions, we obtain a total SO_2 emissions rate of 4,609,108 g per ton of Ni produced. This does not consider sulfur scrubbing or other abatements and is predicated on several assumptions. Moreover, this information does not help in computing other process emissions associated with Ni production from sulfidic ores (such as CO and particulate matter). Hence, we have not provided any process emissions for Ni production in GREET 2022. Based on this, the inventory here may underestimate process emissions, especially for operations without effective emissions controls.

2.3.3 Approach: Laterite Ores

Unlike sulfide ores, the Ni-concentrate equivalent produced from laterite ores usually does not have a fixed Ni content; instead, its Ni content varies with ore grade (Norgate and Jahanshahi, 2011). This means that for sulfide ores, ore grade influences energy and material needs only for the mining and beneficiation stages. In contrast, for laterite ores, ore grade influences these needs for all stages of Ni production (from mining to refining). Previous studies provide equations that capture this variation in life-cycle energy of laterite ore-based Ni production as a function of ore grade, using pyrometallurgical (Equation 11) and hydrometallurgical processing (Equation 12) (Elshkaki et al., 2017; Norgate and Jahanshahi, 2011; Van der Voet et al., 2019). A description of the variables used in these equations is provided in Table 3.

$$LCE_{laterite-Ni,pyro} = 169.53 \times 0G^{-0.607} \tag{11}$$

$$LCE_{laterite-Ni,hydro} = 199.51 \times 0G^{-0.844}$$
(12)

Our literature review did not yield any study on pyrometallurgical processing of Ni from laterite ores, making it impossible to use Equation 11. On the other hand, the life-cycle energy obtained via Equation 12 (for hydrometallurgical processing) is at variance with that calculated for existing LCA studies on this subject (Khoo et al., 2017b, 2017a; Norgate and Jahanshahi, 2011; S. A. Northey et al., 2014). Hence, given the inability to account for a reliable equation that explains the variation in life-cycle or even process energy for laterite-ore based Ni production, we focus on material and energy flows or life-cycle inventory (LCI) for a single ore grade for laterite ores in GREET 2022. Furthermore, given the lack of LCI data on the pyrometallurgical processing of laterite ores in our literature review, we confine ourselves to LCI for the hydrometallurgical processing of these ores in GREET 2022.

The LCI for laterite ore-based Ni production in GREET 2022 is based on Northey et al. (2014) due to its greater coverage compared to other studies analyzed in our literature review (Khoo et al., 2017a, 2017b; S. A. Northey et al., 2014). However, we did not find any stage-wise inventory details for Ni production from laterite ores in any study within our literature review. Hence, we provide a single inventory, encompassing all stages of production (from mining to refining), for laterite ore-based Ni production (provided in Table 8).

Material/Energy Inputs	Values	
Material Inputs (ton/ton of Ni)		
Ammonium nitrate	0.053	
Lime	20	
Ammonia	0.637	
Sulfuric acid	25	
Hydrogen	0.070	
Energy Inputs (mmBtu/ton of Ni)		
Diesel	5.487	
Natural gas	567.501	
Electricity	16.991	

 Table 8: Material and energy flows for laterite-based Ni production

Since ore source (location) influences emission impacts of Ni production, we consider two electric grid mixes in GREET 2022 to account for this influence: one for mining and preparing laterite ores and the other for primary Ni extraction (hydrometallurgical processing) and refining steps. Both grid mixes are different, since like sulfide ores, mining of laterite ores often occurs at different places from those of its processing. The grid mix for laterite ore production is derived based on the share (%) in mine-level laterite-based Ni production of different nations from which the US obtains its Class I Ni supply (including both domestic and imports). Conversely, the grid mix for Ni extraction (via hydrometallurgical processing) and refining is based on the share (%) of different nations in Class I Ni imports by the United States. Table 9 provides both these grid mixes. For GREET 2022, since we do not have a breakup of stage-wise inventory for laterite ore-based Ni production, we use only the grid mix for Ni extraction and refining for all stages, instead of both grid mixes. However, we plan to revisit this in subsequent GREET versions upon obtaining stage-wise LCI for laterite-based Ni production.

Countries	Share in production (%)		
Countries	Nickel ore production	Ni extraction and refining	
Australia	0.00	15.63	
Brazil	5.24	0.10	
Canada	0.00	44.17	
Finland	0.00	9.11	
Japan	0.00	3.09	
New Caledonia	15.23	0.00	
Norway	0.00	11.61	
Russia	0.00	7.85	
China	0.00	0.36	
Indonesia	42.69	0.00	
Philippines	24.30	0.00	
South Africa	0.00	4.44	
Others	12.54	3.64	

Table 9: Grid mixes used for Ni production processes from laterite ores

All inputs and the resultant environmental calculations are provided for nickel (across sulfide and laterite ores) in both Mat_Inputs and Nickel sheets of GREET2.

3 COPPER (Cu)

3.1 Significance, Production and Imports

Like Ni, copper (Cu) consumption has grown substantially over more than 100 years – from 0.5 million metric tons in the year 1900 to ~24.4 million metric tons in 2018 for refined Cu (Henckens and Worrell, 2020; Koppelaar and Koppelaar, 2016; USGS, 2022b). This rise in demand is an outcome of the element's multiple advantageous properties, such as its high electrical and thermal conductivity, large ductility, low susceptibility to corrosion, and ease of recycling. Its beneficial properties have led to Cu becoming the third most important element in the industrial era behind iron and aluminum (Moreau et al., 2021; Sverdrup et al., 2014). Cu is used across a wide range of sectors, encompassing electricity and pipeline infrastructure (or energy), furniture, industrial plant and machinery, construction and buildings, coins, electronics, information networks, and transport (Chen et al., 2019; Dong et al., 2020; S. Northey et al., 2014; Sverdrup et al., 2014). Cu has also become pivotal to the aim of a cleaner, sustainable future amidst the recent spurt for clean energy technologies. These include transmission and distribution (T&D) infrastructure for renewable energy (solar/wind/other sources), secondgeneration photovoltaics like copper-indium-selenide (CIS) or copper-indium-gallium-selenide (CIGS) panels, and energy storage technologies like lithium-ion batteries (LIBs) of which Cu constitutes a considerable weight share (Chen et al., 2019; Dong et al., 2020; S. Northey et al., 2014; Sverdrup et al., 2014). Moreover, Cu use is expected to increase over the next few decades with the ever-increasing global population and its associated need for various forms of infrastructure (Dong et al., 2020). Unlike the other elements analyzed in this report, the United States does not consider Cu a critical mineral (US Department of the Interior, 2022). Nevertheless, given the benefits mentioned above, the robust supply of Cu is essential in helping the US accomplish its goals on energy transition and other initiatives of strategic importance.

Cu ranks 26th in terms of elemental availability in the earth's crust (0.005%), behind Ni but ahead of chromium (Cr) and cobalt (Co) (Henckens and Worrell, 2020; Lossin, 2001). Cu is found in over 200 minerals in notable amounts, of which 20 are significant for its commercial production – these are listed in Table 10; prominent among these are chalcopyrite, bornite, and chalcocite (Lossin, 2001). Cu ores also contain other elements in significant amounts, such as iron (Fe), lead (Pb), tellurium (Te), selenium (Se), antimony (Sb), arsenic (As), gold (Au), and silver (Ag) (Lossin, 2001). Like Ni, Cu is also produced primarily from two types of ores: sulfide and laterite (oxide). Nearly 80% of primary Cu is produced from sulfide ores via pyrometallurgical treatment, with the remaining produced via hydrometallurgical processing of oxide ores (Brinson et al., 2020; Fthenakis et al., 2009; Kuipers et al., 2018; Lossin, 2001).

In this report, our focus is solely on primary (refined) Cu production. In 2018, the United States produced 1.23 million metric tons of Cu, amounting to two-thirds (~68%) of its refined Cu demand for that year (USGS, 2022b). The remaining one-third (32%) share of net imports (exports minus imports of refined Cu) came mainly from Chile, Canada, and Mexico, with a small percentage of other imports from other nations (USGS, 2022b). Table 11 provides the share (%) of refined Cu from different sources in the U.S. Cu consumption mix for 2018 (USGS, 2022b).

Mineral	Chemical composition	Copper (wt.%)
Cuprite	Cu ₂ O	88.8
Chalcocite	Cu ₂ S	79.9
Tenorite	CuO	79.9
Digenite	Cu ₉ S ₅	78.0
Covellite	CuS	66.5
Bornite	Cu_5FeS_4/Cu_3FeS_3	62.6
Atacamite	$CuCl_2.3Cu(OH)_2$	59.5
Malachite	$CuCO_3.Cu(OH)_2$	57.5
Brochantite	CuSO ₄ .3Cu(OH) ₂	56.2
Azurite	$2CuCO_3.Cu(OH)_2$	55.3
Antlerite	CuSO ₄ .2Cu(OH) ₂	53.8
Enargite	Cu ₃ AsS ₄	48.4
Tennantite	$Cu_{12}As_4S_{13}$	47.0
Dioptase	$Cu_{6}[Si_{6}O_{18}].6H_{2}O$	40.3
Tetraedrite	$Cu_{12}Sb_4S_{13}$	37.5
Chalcopyrite	CuFeS ₂	34.6
Chrysocolla	CuSiO ₃ .nH ₂ O	33.0
Chalcanthite	CuSO ₄ .5H ₂ O	25.5
Bournonite	CuPbSbS ₃	13.0

 Table 10: Major Cu-containing minerals (reproduced from (Lossin, 2001))

Table 11: Share (%) of different nations in US consumption mix of refined Cu (obtained from (USGS, 2022b))

Country	Share (%) of refined Cu production			
	All ores	Sulfide ores	Laterite ores	
US	67.69	59.80	81.58	
Canada	7.14	11.15	0.00	
Chile	20.06	22.87	15.18	
Mexico	2.62	3.04	1.91	
Others	2.49	3.14	1.33	
Share (%) of production from different ores: Sulfide: 64.21%; Laterite: 35.79%				

USGS (2022b) also provides data on mine-level Cu production from different nations. As for Ni, the supply chain for Cu production is highly globalized, where element mining and processing are often undertaken at different locations. Therefore, accounting for these locational differences is a highly challenging endeavor. Hence, in GREET 2022, we assume that all nations that supply Cu to meet the US demand (including the US itself and import sources) only process the Cu mined domestically in their respective geographies. Based on this assumption, Table 11 lists the share of different sources (domestic and import) in the refined Cu supply mix of the US for both sulfide and laterite ores, along with a breakup of total Cu contribution from these ore types.

3.2 Copper Production Process

A previously published Argonne report provides details on the processing methodology for Cu production from both sulfidic and laterite ores (Benavides et al., 2015). We briefly summarize these details here for the benefit of readers. Figures 3 and 4 show the respective process flows for Cu production from sulfide and laterite ores, respectively. Broadly, Cu production from these ores is similar to process flows for Ni production from the corresponding ore type.



Figure 4: Schematic of Cu production from laterite ores

3.2.1 Copper Production: Sulfide Ore

Unlike Ni, the domination of sulfide ores in global Cu production is both due to the wider presence of Cu-containing sulfidic minerals across the globe and their relatively higher ore grades (or better economic feasibility of Cu extraction from sulfidic ores) (Kuipers et al., 2018; Lossin, 2001; Mudd et al., 2013). The process of producing sulfide ore-based Cu is described

below, based on a number of references (Brinson et al., 2020; Lossin, 2001), and is shown in Figure 3.

Cu is mined from either open pit or underground mines, with open pit mining being the standard of mining due to most mines having lower Cu concentrations. Extracted ore is crushed and milled into fine particles to ease the separation of different mineral phases and gangue. The ore is beneficiated via froth flotation to remove gangue, and the valuable minerals are separated off as froth. Froth flotation involves the use of organic reagents as collectors (e.g., xanthates), modifiers (reagent typically has hydroxyl ions), and stabilizers (alcohols). Beneficiation is generally a multi-step process, at the end of which *Cu concentrate* (25-35 wt.% Cu) is obtained. This *Cu concentrate* is ready for pyrometallurgical processing.

Pyrometallurgical processing of Cu involves roasting, smelting, and converting steps. While these three steps were conducted separately till about the 1970s, present-day Cu production combines the roasting and smelting steps into a single process, after which converting is conducted separately. Roasting is only separated from the smelting process in case of older plants and/or when there is a need to remove specific elements (such as Fe, As, and sulfur or S). Several smelting technologies have been developed over the years. The most commonly used smelting process in present-day Cu production is *flash smelting*, where air (oxygen) is introduced in large quantities to partially oxidize Cu concentrate. Iron sulfide oxidizes to form iron oxide, which is separated via reaction with silica as slag, while copper sulfide is retained almost entirely in the final output (Cu matte, 40-70%). These reactions also produce sulfur dioxide (SO₂) and heat, which makes the smelting operation autogenous or near-autogenous (i.e., it does not require much external energy input). The advantages of autogenous smelting include a high reaction rate (and thereby, high matte production rate), energy and cost savings, and high SO₂ concentration (which can be easily used to produce useful products like sulfuric acid). Cu matte output is then converted (or blown with air blasts in molten state) to oxidize it to crude Cu, ferrosilicate slag, and SO₂. Conversion generally occurs in two steps: the first step yields copper sulfide (75-80% Cu), and the next step yields blister copper (98-99% Cu, where the blister refers to SO₂ blisters contained in the produced metal). The most commonly used converter is the Peirce-Smith converter, used for over 80% of global Cu production. Like smelting, conversion also produces slag and SO₂. However, while smelting is usually a continuous process, converting is typically a batch process.

The last step is refining, which is of three types: pyrometallurgical/fire, electrolytics, and remelting of cathodes and shape casting. The refining process used depends mainly on the desired purity level of Cu. Pyrometallurgical refining involves similar processes as smelting/converting, i.e., removing impurities (as slags), sulfur (to < 0.0005 wt.% as SO₂), and oxygen in the metal. Examples of pyrometallurgical refining include fire refining (continuous or discontinuous) to produce the final refined Cu, and anode casting, where Cu is obtained as anodes on pure Cu molds and refined further. Electrolytic refining is the most common refining technique, used for 80% of global Cu production (both primary and secondary Cu) to reduce impurities and precious metals (such as Se and Te). This refining is conducted in electrolytic cells that use Cu or stainless-steel sheets as cathodes, cast Cu (from anode casting) as anodes, and a combination of Cu and sulfuric acid as electrolyte. Waste is produced as anode slime on the bottom of cells, which is processed further to extract other precious elements. Cu cathode

from electrolytic refining (99.97-99.99 wt.% Cu) is then remelted and cast in special furnaces (to produce them in desired shapes) or atomized into powders as needed.

3.2.2 Copper Production: Laterite Ore

Details on laterite-ore based Cu production are given below, based on multiple references (Brinson et al., 2020; Lossin, 2001; Northey et al., 2013; Yang et al., 2022), while Figure 4 shows the schematic for Cu production from these ores. The differences in laterite ore processing vis-à-vis their sulfidic counterparts are mainly during the beneficiation and material extraction stages. Instead of common beneficiation techniques used for sulfide ores (such as magnetic separation and froth flotation), laterite ores are mined and then treated via hydrometallurgical methods. A typical hydrometallurgical treatment involves three steps: (a) Leaching, which is usually done via heap leaching (ore is crushed, stacked to heaps, reacted with dilute sulfuric acid, and the acid trickles down to dissolve Cu); (b) Solvent extraction (where the leached solution is mixed with an organic solution to extract Cu in organic phase and separate it from iron in aqueous phase, followed by the reaction of Cu with sulfuric acid to enrich the acid with Cu); and (c) Electrowinning (where copper-enriched sulfuric acid is sent to electrowinning cells to get Cu on stainless steel sheet cathodes, with water splitting reaction occurring at the anode to emit hydrogen and oxygen). Electrowinning is equivalent to refining, so the final Cu produced is cathode copper (99.99 wt.% Cu) and does not have to be refined separately.

3.3 Material and Energy Flows for Copper Production

3.3.1 Context of Update

As in the case of Ni, multiple studies have highlighted the temporal decline in Cu ore grade till date, as well as the likely continuation of this trend due to its expected high demand in the future (Koppelaar and Koppelaar, 2016; Northey et al., 2013; S. Northey et al., 2014; Sverdrup et al., 2014). This is expected to significantly influence the costs, input material and energy needs, and the resultant environmental impacts of primary Cu production with time. Also, the US has consistently shown about 30-40% import dependence over the past few years to meet its refined Cu needs (USGS, 2022a). This makes the location of Cu production significant, given its effect on the environmental impacts of the United States' Cu supply mix (for reasons related to the nature of electric grid mix, as well as environmental regulations enforced in specific sources of production). Thus, like for Ni, ore grade, ore type, and production location are critical to Cu's environmental profile and must be considered for its holistic environmental analysis.

GREET 2021 provides Cu inventory as a single inventory across all ore grades and ore types for two locations: the United States and Chile (Wang et al., 2021). In GREET 2022 (Wang et al., 2022), we provide the LCI for Cu consumed in the US as a function of ore grade, type, and production location, based on data available in our literature review.

3.3.2 Approach Used: Sulfide Ores

As for Ni, we have provided LCI for Cu production as a function of ore grade (wt.% Cu content in ore) and the location of Cu production (from mining to refining/electrowinning).

Like Ni, literature shows that ore grade influences material and energy needs for only mining and beneficiation stages, given the fixed Cu content of *Cu concentrate* from the beneficiation step (Dong et al., 2020; Northey et al., 2013). Our literature review did not yield any study that analyzed the trends for amounts of different input materials used for mining and beneficiation stages as a function of ore grade. However, literature does report an equation that explains the variation in process energy requirements with ore grade (Equation 13) (Kuipers et al., 2018; Northey et al., 2013). The description of variables used in this equation and other equations used below in this subsection are provided in Table 12.

$$PE_{Mining+Beneficiation,Cu-S} = 15.697 \times OG (Cu-S)^{-0.573}$$
(13)

Our literature review also yielded several studies that evaluate the life-cycle environmental impacts of Cu production from sulfide ores (Dong et al., 2020; Kulczycka et al., 2016; Northey et al., 2013; Sanjuan-Delmás et al., 2022; Wang et al., 2015). Among these, Sanjuan-Delmás et al. (2022) provide the most recent and exhaustive LCI, encompassing the different stages of Cu production (mining, beneficiation, Cu extraction via pyrometallurgy, and refining). Similar to Ni, we have used data from Sanjuan-Delmás et al. (2022) along with some assumptions to account for the effect of Cu ore grade on energy requirements of mining and beneficiation stages. The relevant equations for this exercise are provided below (Equations 14-37), while the variables used in these equations are described in Table 12.

We first considered the LCI provided for Cu production in Sanjuan-Delmás et al. (2022). This study provides us three major datasets (similar to those considered for Ni-related calculations): (a) Total process energy ($PE_{Mining+Beneficiation,Cu-S,Ref}$) of 50.258 mmBtu/ton consumed across both mining and beneficiation of Cu from sulfide ores; (b) Shares (%) of mining ($Share_{PE,Mining,Cu-S,Ref}$) and beneficiation ($Share_{PE,Beneficiation,Cu-S,Ref}$), obtained using Equations 14 and 15 as 36.75% and 63.25% respectively; and (c) The share (%) of different energy sources (residual oil, diesel, natural gas, LPG, and electricity) in process energy consumed for these stages, computed for Sanjuan-Delmás et al. (2022) using Equations 16-25. Table 12 describes these various variables and their respective values; note that all these values are provided for a Cu sulfide ore with an ore grade of 0.18% (Sanjuan-Delmás et al., 2022).

Variables	Description
Cu-S	Refers to copper production from sulfide ores
$PE_{Mining+Beneficiation,Cu-S}$	Total process energy used across both mining and beneficiation stages
PE _{Mining+Benef} iciation,Cu-S,Ref	Total process energy used across both mining and beneficiation of sulfidic copper ores, as obtained from (Sanjuan-Delmás et al., 2022), is 50.258 mmBtu/ton
PE _{Mining,Cu-S,Ref}	Process energy consumed for the mining of sulfidic copper ores, as obtained from (Sanjuan-Delmás et al., 2022)
Share _{PE,Mining,Cu-S,Ref}	Share (%) of process energy consumed for the mining of sulfidic copper ores from total process energy consumed across both mining and beneficiation stages, as obtained from (Sanjuan-Delmás et al., 2022) (value: 36.75%)
PE _{Beneficiation,Cu-S,Ref}	Process energy consumed for the beneficiation of sulfidic copper ores, as obtained from (Sanjuan-Delmás et al., 2022)
Share _{PE,Benef} iciation,Cu–S,Ref	Share (%) of process energy consumed for the beneficiation of sulfidic copper ores from total process energy consumed across both mining and beneficiation stages, as obtained from (Sanjuan-Delmás et al., 2022) (value: 63.25%)
PE _{Residual oil,Mining,Cu-S,Ref}	Residual oil-based process energy consumed during the mining of sulfidic copper ores, as per (Sanjuan- Delmás et al., 2022)
Share _{Residual oil,Mining,Cu–S}	Share (%) of residual oil in total process energy consumed during the mining of sulfidic copper ores (value: 0%)
PE _{Diesel,Mining,Cu-S,Ref}	Diesel-based process energy consumed during the mining of sulfidic copper ores, as per (Sanjuan-Delmás et al., 2022)
Share _{Diesel,Mining,Cu-S}	Share (%) of diesel in total process energy consumed during the mining of sulfidic copper ores (value: 80.99%)
PE _{Natural} gas,Mining,Cu–S,Ref	Natural gas-based process energy consumed during the mining of sulfidic copper ores, as per (Sanjuan- Delmás et al., 2022)
Share _{Natural} gas,Mining,Cu–S	Share (%) of natural gas in total process energy consumed during the mining of sulfidic copper ores (value: 0.55%)
PE _{LPG,Mining,Cu-S,Ref}	Liquefied petroleum gas (LPG)-based process energy consumed during the mining of sulfidic copper ores, as per (Sanjuan-Delmás et al., 2022)
Share _{LPG,Mining,Cu-S}	Share (%) of LPG in total process energy consumed during the mining of sulfidic copper ores (value: 0%)
PE _{Electricity,Mining,Cu-S,Ref}	Electricity-based process energy consumed during the mining of sulfidic copper ores, as per (Sanjuan-Delmás et al., 2022)
Share _{Electricity,Mining,Cu-S}	Share (%) of electricity in total process energy consumed during the mining of sulfidic copper ores (value: 18.46%)

Table 12: Description of variables used to compute process energy needs for Cu production from sulfidic ores as a function of ore grade
Table 12	(Cont.)
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Variables	Description		
PE _{Residual} oil,Beneficiation,Cu–S,Ref	Residual oil-based process energy consumed during the beneficiation of sulfidic copper ores, as per (Sanjuan-Delmás et al., 2022)		
Share _{Residual} oil,Beneficiation,Cu–S	Share (%) of residual oil in total process energy consumed during the beneficiation of sulfidic copper ores (value: 0%)		
PE _{Diesel,Beneficiation,Cu-S,Ref}	Diesel-based process energy consumed during the beneficiation of sulfidic copper ores, as per (Sanjuan-Delmás et al., 2022)		
Share _{Diesel,Benef} iciation,Cu–S	Share (%) of diesel in total process energy consumed during the beneficiation of sulfidic copper ores (value: 0%)		
PE _{Natural} gas,Beneficiation,Cu–S,Ref	Natural gas-based process energy consumed during the beneficiation of sulfidic copper ores, as per (Sanjuan-Delmás et al., 2022)		
Share _{Natural} gas,Beneficiation,Cu–S	Share (%) of natural gas in total process energy consumed during the beneficiation of sulfidic copper ores (value: 0.35%)		
PE _{LPG,Benef} iciation,Cu-S,Ref	Liquefied petroleum gas (LPG)-based process energy consumed during the beneficiation of sulfidic copper ores, as per (Sanjuan-Delmás et al., 2022)		
Share _{LPG,Benef} iciation,Cu–S	Share (%) of LPG in total process energy consumed during the beneficiation of sulfidic copper ores (value: 0%)		
PE _{Electricity} ,Beneficiation,Cu-S,Ref	Electricity-based process energy consumed during the beneficiation of sulfidic copper ores, as per (Sanjuan-Delmás et al., 2022)		
Share _{Electricity} ,Beneficiation,Cu–S	Share (%) of electricity in total process energy consumed during the beneficiation of sulfidic copper ores (value: 99.65%)		
PE _{Mining,Cu-S}	Process energy used for the mining of sulfidic copper ores (calculated for different ore grades)		
PE _{Beneficiation,Cu-S}	Process energy used for the beneficiation of sulfidic copper ores (calculated for different ore grades)		
PE _{Residual oil,Mining,Cu-S}	Residual oil-based process energy consumed during the mining of sulfidic copper ores (calculated for different ore grades)		
PE _{Diesel,Mining,Cu-S}	Diesel-based process energy consumed during the mining of sulfidic copper ores (calculated for different ore grades)		
PE _{Natural gas,Mining,Cu-S}	Natural gas-based process energy consumed during the mining of sulfidic copper ores (calculated for different ore grades)		
PE _{LPG,Mining,Cu-S}	LPG-based process energy consumed during the mining of sulfidic copper ores (calculated for different ore grades)		
PE _{Electricity,Mining,Cu-S}	Electricity-based process energy consumed during the mining of sulfidic copper ores (calculated for different ore grades)		

Table	12	(Cont.)
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PE _{Residual oil,Beneficiation,Cu-S}	Residual oil-based process energy consumed during the beneficiation of sulfidic copper ores (calculated for different ore grades)
PF	Diesel-based process energy consumed during the beneficiation of sulfidic copper ores (calculated for
^I ^L Diesel,Beneficiation,Cu–S	different ore grades)
DE	Natural gas-based process energy consumed during the beneficiation of sulfidic copper ores (calculated
¹ ^L Natural gas,Beneficiation,Cu–S	for different ore grades)
DE	LPG-based process energy consumed during the beneficiation of sulfidic copper ores (calculated for
I LPG,Beneficiation,Cu–S	different ore grades)
DF	Electricity-based process energy consumed during the beneficiation of sulfidic copper ores (calculated
¹ ^L Electricity,Beneficiation,Cu–S	for different ore grades)

$$Share_{PE,Mining,Cu-S,Ref} = \frac{PE_{Mining,Cu-S,Ref}}{PE_{Mining+Beneficiation,Cu-S,Ref}}$$
(14)

$$Share_{PE,Beneficiation,Cu-S,Ref} = \frac{PE_{Beneficiation,Cu-S,Ref}}{PE_{Mining+Beneficiation,Cu-S,Ref}}$$
(15)

$$Share_{Residual\ oil,Mining,Cu-S} = \frac{PE_{Residual\ oil,Mining,Cu-S,Ref}}{PE_{Mining,Cu-S,Ref}}$$
(16)

$$Share_{Diesel,Mining,Cu-S} = \frac{\frac{PE_{Diesel,Mining,Cu-S,Ref}}{PE_{Mining,Cu-S,Ref}}$$
(17)

$$Share_{Natural gas, Mining, Cu-S} = \frac{PE_{Natural gas, Mining, Cu-S, Ref}}{PE_{Mining, Cu-S, Ref}}$$
(18)

$$Share_{LPG,Mining,Cu-S} = \frac{\frac{PE_{LPG,Mining,Cu-S,Ref}}{PE_{Mining,Cu-S,Ref}}$$
(19)

$$Share_{Electricity,Mining,Cu-S} = \frac{PE_{Electricity,Mining,Cu-S,Ref}}{PE_{Mining,Cu-S,Ref}}$$
(20)

$$Share_{Residual \ oil, Beneficiation, Cu-S} = \frac{PE_{Residual \ oil, Beneficiation, Cu-S, Ref}}{PE_{Beneficiation, Cu-S, Ref}}$$
(21)

$$Share_{Diesel,Beneficiation,Cu-S} = \frac{PE_{Diesel,Beneficiation,Cu-S,Ref}}{PE_{Beneficiation,Cu-S,Ref}}$$
(22)

$$Share_{Natural gas, Beneficiation, Cu-S} = \frac{PE_{Natural gas, Beneficiation, Cu-S, Ref}}{PE_{Beneficiation, Cu-S, Ref}}$$
(23)

$$Share_{LPG,Beneficiation,Cu-S} = \frac{\frac{PE_{LPG,Beneficiation,Cu-S,Ref}}{PE_{Beneficiation,Cu-S,Ref}}$$
(24)

$$Share_{Electricity,Beneficiation,Cu-S} = \frac{PE_{Electricity,Beneficiation,Cu-S,Ref}}{PE_{Beneficiation,Cu-S,Ref}}$$
(25)

$$PE_{Mining,Cu-S} = PE_{Mining+Beneficiation,Cu-S} \times Share_{Mining,Cu-S,Ref}$$
(26)

$$PE_{Beneficiation,Cu-S} = PE_{Mining+Beneficiation,Cu-S} \times Share_{Beneficiation,Cu-S,Ref}$$
(27)

$$PE_{Residual\ oil,Mining,Cu-S} = PE_{Mining,Cu-S} \times Share_{Residual\ oil,Mining,Cu-S}$$
(28)

$$PE_{Diesel,Mining,Cu-S} = PE_{Mining,Cu-S} \times Share_{Diesel,Mining,Cu-S}$$
(29)

$$PE_{Natural gas, Mining, Cu-S} = PE_{Mining, Cu-S} \times Share_{Natural gas, Mining, Cu-S}$$
(30)

$$PE_{LPG,Mining,Cu-S} = PE_{Mining,Cu-S} \times Share_{LPG,Mining,Cu-S}$$
(31)

$$PE_{Electricity,Mining,Cu-S} = PE_{Mining,Cu-S} \times Share_{Electricity,Mining,Cu-S}$$
(32)

 $PE_{Residual oil,Beneficiation,Cu-S} = PE_{Beneficiation,Cu-S} \times Share_{Residual oil,Beneficiation,Cu-S}$ (33)

$$PE_{Diesel,Beneficiation,Cu-S} = PE_{Beneficiation,Cu-S} \times Share_{Diesel,Beneficiation,Cu-S}$$
(34)

 $PE_{Natural gas, Beneficiation, Cu-S} = PE_{Beneficiation, Cu-S} \times Share_{Natural gas, Beneficiation, Cu-S}$ (35)

$$PE_{LPG,Beneficiation,Cu-S} = PE_{Beneficiation,Cu-S} \times Share_{LPG,Beneficiation,Cu-S}$$
(36)

 $PE_{Electricity,Beneficiation,Cu-S} = PE_{Beneficiation,Cu-S} \times Share_{Electricity,Beneficiation,Cu-S}$ (37)

Like for Ni, we consider six ore grades for analysis in GREET2 (0.5%, 1%, 1.5%, 2%, 2.5%, and 3%), apart from that in Sanjuan-Delmás et al. (2022). Next, we assume that Equation 13 reflects the variation in total process energy used across both mining and beneficiation stages ($PE_{Mining+Beneficiation.Cu-S}$) as a function of ore grade (OG(Cu-S)) (Kuipers et al., 2018; Northey et al., 2013). To disaggregate this total $(PE_{Mining+Beneficiation,Cu-S})$ into separate mining and beneficiation-related energy requirements, we assume that the following parameters for all ore grades are the same as that obtained using Sanjuan-Delmás et al. (2022): (a) Share of mining (Share_{PE,Mining,Cu-S,Ref}) and beneficiation ($Share_{PE,Beneficiation,Cu-S,Ref}$) in the total process energy consumed across both stages ($PE_{Mining+Beneficiation,Cu-S}$); and (b) Share of different energy sources in the process energy consumed separately for mining and beneficiation stages (given in Table 12). We combine these assumptions with a two-step process to obtain fuel-wise and total process energy requirements for individual mining and beneficiation stages. The steps are: (a) Using Equations 26 and 27 to compute the process energy for mining and beneficiation stages separately for different ore grades ($PE_{Mining,Cu-S}$ and $PE_{Beneficiation,Cu-S}$ respectively) as a product of total energy consumed across both stages $(PE_{Mining+Beneficiation,Cu-S})$ and their respective shares in this energy value ($Share_{PE,Mining,Cu-S,Ref}$ and Share_{PE,Beneficiation,Cu-S,Ref} respectively); (b) Use the mixes provided for mining and

beneficiation, *cu-s, Ref* respectively), (b) Ose the linkes provided for hinning and beneficiation stages (given in Table 12) to determine the amount of energy used from different sources for these stages (calculated using Equations 28-37). Table 13 provides the energy inputs for mining and beneficiation steps for the different ore grades considered in GREET 2022.

One grade $(9/)$	Energy inputs (mmBtu/ton)				
Ore grade (%)	Mining	Beneficiation			
0.18%	18.470	31.787			
0.50%	7.373	12.690			
1.00%	4.956	8.530			
1.50%	3.929	6.762			
2.00%	3.332	5.734			
2.50%	2.932	5.046			
3.00%	2.641	4.545			

Table 13: Energy inputs for mining and beneficiation of sulfidic Cu ores for different ore grades (based on (Kuipers et al., 2018; Northey et al., 2013; Sanjuan-Delmás et al., 2022))

Our literature review did not provide any study or analysis on variation in material use for either mining or beneficiation stages for Cu production as a function of ore grade. Hence, for these two stages, we use the material input inventory from Sanjuan-Delmás et al. (2022) and apply it to all ore grades due to the lack of suitable data. We intend to address this aspect in subsequent versions of GREET, subject to data availability.

Post-beneficiation, material inputs are independent of the initial ore grade (Dong et al., 2020; Northey et al., 2013). Hence, we use material and energy LCI from Sanjuan-Delmás et al. (2022) for the remaining stages of Cu production (pyrometallurgical production/smelting and refining). Note that the use of material inventory in GREET 2022 (Wang et al., 2022) makes it different from GREET 2021 (Wang et al., 2021), which does not consider this aspect. Table 14 provides the energy inputs for post-beneficiation Cu pyrometallurgical processing and refining, while Table 15 shows the material inputs for all steps of Cu production.

Table 14: Energy inputs for pyrometallurgical production (smelting) and refining of Cu (based on (Sanjuan-Delmás et al., 2022))

Energy source	Value of input (mmBtu/ton)
Residual oil	1.039
Diesel	0.076
Natural gas	0.000
Coal	0.000
Gasoline	0.002
LPG	0.033
Electricity	5.669

M-4	Input quantities (US ton/US ton of copper)			
Material inputs	Mining	Beneficiation	Smelting	
Ammonium nitrate	0.375			
Lime	0.118		0.0084	
Road salt	0.021		3.661×10^{-4}	
Salt solution	0.001			
Silica			0.256	
Limestone			0.016	
Oxygen			0.705	
Soda (Sodium carbonate)			7.189×10^{-4}	
Baryte (BaSO ₄)			0.0015	
Liquid caustic soda (50% NaOH)			7.440×10^{-2}	
Sodium hydroxide (99% NaOH)			$8.049 imes 10^{-5}$	
Ammonia (99.9%) (Compressed gas)			0.0046	
Caustic ammonia (25% aqueous solution)			1.350×10^{-5}	
Graphite electrodes			2.000×10^{-4}	
Iron powder			1.039×10^{-5}	
Chlorine			3.635×10^{-5}	
Copper powder			2.648×10^{-4}	
Nitric acid (65% HNO ₃)			1.817×10^{-4}	
Hydrochloric acid (37% HCl)			7.270×10^{-5}	
Hydrogen peroxide (50% H ₂ O ₂)			0.0024	

Table 15: Material inputs for all stages of Cu production from sulfide ores (based on (Sanjuan-Delmás et al., 2022))

Along with ore grade, the location of mining and subsequent processing of Cu is also influential on the resultant environmental impacts. However, unlike Ni, we could not obtain disaggregated data on the actual location of different steps for producing Cu from sulfidic ores. Hence, we assume that the location mix of refined Cu in the U.S. consumption mix (Table 11) for sulfidic ores also represents the electric grid mix used to process and produce this element.

3.3.3 Approach Used: Laterite Ores

Lateritic Cu ores are processed predominantly via hydrometallurgical methods and do not require any concentrate (unlike *Cu concentrate* in the case of sulfidic ores). This indicates that variation in ore grade influences the entire chain of Cu production from an environmental perspective, instead of only mining and beneficiation stages for sulfidic ores. Our literature review did not yield any equation or study that analyzes this variation in process energy input, material requirements, or life-cycle energy of laterite ore-based Cu production. Hence, we consider inventory flows for lateritic Cu production from Yang et al. (2022), as it has the most recent LCI on this topic. We intend to revisit this inventory and account for its variation with ore grade in subsequent GREET versions. Table 16 provides the material and energy inputs for Cu production from laterite ores. In addition, to account for variations in the location of lateritic Cu production, we assume the mix of laterite-based Cu from different nations (Table 11) as the electric grid mix of its production.

Table 16: Material and energy inputs for all stages of Cu production from laterite ores (based on Yang et al. (2022))

Material inputs	Input quantities (US ton/US ton of copper)
Ammonium nitrate	0.03
Sulfuric acid	2.6
Cobalt sulfate	0.0004
Energy inputs (ton/ton)	
Energy source	Input value (mmBtu/ton)
Diesel	0.669
Electricity	12.008

All the LCI and other details for sulfidic and laterite ores of copper are provided in Mat_Inputs and Copper sheets of GREET2.

4 TITANIUM (Ti)

4.1 Significance, Production, and Imports

Titanium (Ti) is a relatively abundant element in the earth's crust, with its availability being higher than that of copper (Cu) and nickel (Ni) but much lower than of iron (Free, 2020; Sibum et al., 2017; Zhang et al., 2011). Ti is used in a variety of forms, including as sponge metal, ingots, powders, alloys, and structural material, across multiple sectors (Gao et al., 2018; Zhang et al., 2011). The most common form of Ti use is in titanium dioxide (TiO₂) form as a pigment, as filler in paper, rubber, and plastic, and as a flux for manufacturing glass (Middlemas et al., 2015; Sibum et al., 2017; Zhang et al., 2011). Ti is also used in alloy and metallic forms for applications in aerospace, defense, healthcare, and petrochemical sectors due to its advantageous properties like low density, high specific strength, strong resistance to high temperature and corrosion, and good biocompatibility (Middlemas et al., 2015; Sibum et al., 2020, 2011).

Ti exists in a wide range of forms inside the earth's crust. Primary Ti is found in igneous rocks as ilmenite (FeTiO₃) and perovskite (CaTiO₃), while intermediate Ti exists as a basic element in zircon minerals and silicates (Free, 2020; Perks and Mudd, 2019; Sibum et al., 2017). Ti is also found in two TiO₂ forms – anatase (metastable tetragonal TiO₂) and brookite (orthorhombic TiO₂) – in metamorphic deposits (ref). Secondary Ti deposits are found in ilmenite deposits and sands that are widely distributed in coastal regions, and in clays as TiO₂ (Free, 2020; Perks and Mudd, 2019; Sibum et al., 2017; Zhang et al., 2011). While ilmenite is the leading resource of TiO₂ production, rutile (the most common form of tetragonal TiO₂) is the preferred resource for producing Ti and its compounds (Free, 2020; Perks and Mudd, 2019; Sibum et al., 2017). Typically, rutile reserves are processed to produce Ti sponge metal, which is the raw material for producing subsequent forms of Ti, including ingot, powder, and alloys (Free, 2020; Perks and Mudd, 2019; Sibum et al., 2017; Zhang et al., 2011).

The United States Geological Survey (USGS) does not provide data on Ti production in the US (in any form). However, the USGS does identify a substantial import dependence (>50%) of the US for sponge metal from 2016 to 2021 (USGS, 2022a). Assuming the US Ti sponge metal capacity as production quantity, we estimate that the US would need to meet ~70% of its sponge metal needs via imports, which came almost entirely from Japan (88%) and Kazakhstan (10%) (USGS, 2022a, 2022b). This strong import dependence, the low sponge metal production capacity in the US, and the substantial need of Ti for various sectors, have led to its classification as a *critical mineral* by the United States (US Department of the Interior, 2022).

Unlike sponge metal, USGS data indicates that the US meets almost all its Ti ingot needs (~98.5%) via domestic production, using both domestic and imported sponge (USGS, 2022b). A similar scenario is seen for Ti powders, whose large exports (vis-à-vis imports) in 2020 indicate that its needs in the US are also met through domestic production (USGS, 2022b). Table 17 shows the share of domestic and import sources in Ti production (sponge metal and ingot), while Table 18 shows the share of different nations in the imports of Ti sponge metal and ingot.

Sources	Share (%) of sponge metal production	Share (%) of ingot production
Domestic	30.4	98.5
Imports	69.6	1.5

Table 17: Share of domestic and import sources in Ti production (based on (USGS, 2022a, 2022b))

Table 18: Import distribution by different sources (nations) (based on (USGS, 2022a, 2022b))

Sources	Share (%) of sponge metal imports	Share (%) of ingot imports
Japan	88.5	
Kazakhstan	9.8	18.6
Poland	0.4	72.8
Russia	0.2	
Ukraine	1.0	
Others	0.2	8.6

4.2 Production Processes for Ti Sponge Metal and Powders

Ti metal is typically produced from titanium chloride (TiCl₄), which is generated through the chlorination of Ti ore concentrate (Free, 2020; Gao et al., 2018; Sibum et al., 2017). The most preferred feedstock for TiCl₄ production is natural rutile (95% TiO₂), but its low presence (only 10% of global Ti feedstock needs) limits its use (Perks and Mudd, 2019; Xia et al., 2020; Zhang et al., 2011). Hence, the typical process is to produce Ti metal using synthetic rutile produced from titanium slag. Figure 5 shows the schematic for producing Ti sponge metal, ingots, and powders using this resource (Gao et al., 2018; Serres et al., 2011; Sibum et al., 2017). A description of the processes used for Ti production in various forms is given below, based on multiple references (Free, 2020; Gao et al., 2018; Perks and Mudd, 2019; Serres et al., 2011; Sibum et al., 2017; Xia et al., 2020; Zhang et al., 2011).

Ilmenite ore is extracted from earth and then processed into ilmenite concentrate by separating iron ore from it using high-intensity magnetic separation and flotation. This concentrate is blended with petroleum coke (reducing agent) and pitch (bonding agent) and smelted in an electric furnace. Smelting causes iron to separate and produces high-grade titania slag (good quality slag with high TiO₂ content). Next, titania slag is mixed in a chlorination furnace with petroleum coke to produce crude titanium tetrachloride (TiCl₄), which is refined further to obtain high-purity TiCl₄. This high-grade TiCl₄ is reduced with magnesium (Mg) and treated using vacuum distillation to produce Ti sponge metal, while the magnesium chloride (MgCl₂) produced via this reaction is subjected to an auxiliary electrolysis process to produce Mg and chlorine (Cl). While Mg is recycled back to the reduction and distillation of TiCl₄, Cl is recycled back to the chlorination process, indicating closed-loop recycling of both elements. However, make-up quantities of Mg and Cl are also needed, as closed-loop recycling is not 100% efficient.





Despite their high purity (99.5-99.6% Ti), sponge metal does not exhibit satisfactory mechanical properties (Serres et al., 2011; Sibum et al., 2017). Hence, it is converted to Ti ingots using a vacuum arc remelting (VAR) process to obtain Ti metal and alloys with high purity and chemical homogeneity. VAR uses consumable electrodes made using a combination of Ti sponge metal, scrap, and alloying elements that are all welded using plasma or metal-inert gas welding (Serres et al., 2011; Sibum et al., 2017). The electrodes are melted at high vacuum pressure, with the necessary heat provided by an electric arc between the electrode and the ingot. The molten metal solidifies upon coming into contact with copper crucibles cooled by water to obtain the final ingot. These ingots can be used to produce semi-fabricated products and Ti castings through hot forging and machining.

Ti powder is typically produced via the atomization of ingots in the liquid phase (Serres et al., 2011). Ti is melted in a crucible and passed through a tube that splits it into different jets using gas flow, with the droplets solidified into powders. Typically, this process is conducted under argon flow, with a couple of hours needed for melting and atomizing Ti.

4.3 Material and Energy Flows for Ti Production

Table 19 shows the material and energy inputs and emission outputs for Ti production, based on (Gao et al., 2018) for sponge metal production and (Serres et al., 2011) for the production of Ti ingots and powders. We combine these material and energy flows with the shares of sponge metal and ingot production sources for the Ti supply chain in the United States (provided in Tables 17 and 18). All data is provided in Titanium sheet of GREET2.

Motoriala/	Ti sponge metal production			Ti powder production				
Energy Sources	Ore mining and dressing	Ti slag smelting	Chlorination and refining	Reduction and distillation	Electrolysis of MgCl ₂	Ingot formation	Forged Ti production	Ti powder production
Material Outp	outs (ton of inter	mediate output	/product)					
Ti sponge				1				
Ti ingot						1		
Forged Ti							1	
Ti powder								1
MgCl ₂				3.977				
Material Input	s (ton/ton of inte	rmediate prod	uct)					
Ti sponge						1.02		
Ti ingot							1.08	
Forged Ti								1.081
Raw ore	91.1							
Water	30.1		0.44					
Floatation								
agent	0.034							
Pitch		0.279						
Petroleum								
coke		0.502	0.651					
Graphite		0.067						
Sodium								
hydroxide			4.52					
Magnesium				0.044				
(Back-up)				0.041				
Chlorine			1.60					
(Back-up)			1.62		0.070			
Sulfuric acid					0.070			0.005
Argon		e• 4 • • 4						0.295
Energy Inputs	(mmBtu/US ton	of intermediat	e output)		1			
Diesel	0.589	20.686	30.943					
Natural gas	0.000	0.942	2.883					
Coal	0.008	0.207	/9.923	15 001	11.0.10	12 010	21.200	0.070
Electricity	3.247	14.539	7.882	15.001	44.849	13.919	21.280	9.279

 Table 19: Material and energy flows for Ti production (sponge metal, ingot, and powder) (Gao et al., 2018; Serres et al., 2011)

5 RARE-EARTH ELEMENTS (REEs)

5.1 Significance, Production and Imports

REEs refer to a group of 17 elements in the Periodic Table that constitute the "lanthanide group" (atomic nos.: 57 to 71), along with yttrium (atomic no.: 39) and scandium (atomic nos.: 21). These elements have similar and unique physical and chemical properties and distinctive structure (4f orbitals) (Vahidi and Zhao, 2017). This has led to their use in many high-tech industries/products, such as wind turbines (magnets), optics, fluorescent lighting (phosphors), ceramics, lasers, defense systems, catalytic converters, and hybrid and electric vehicles (rechargeable batteries and magnets) (Balaram, 2019; Zaimes et al., 2015). The use of REEs in such a vast range of sectors, especially in green energy and energy efficiency technologies, has led to most of these REEs being classified as a *critical mineral* in the United States (US Department of the Interior, 2022; US DOE, 2020). REEs are classified into three groups based on their weights as light, medium, and heavy rare-earth elements. Table 20 shows the various REEs classified under these three groups.

Group	Rare Earth Element		
Light Para Forths (LREFs)	Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium		
Light Rare-Earths (LREES)	(Nd), Promethium (Pm)		
Medium Rare-Earths (MREEs)	Samarium (Sm), Europium (Eu), Gadolinium (Gd)		
Heavy Rare-Earths (HREEs)	Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er),		
	Thulium (Tm), Ytterbium (Yb), Lutetium (Lu)		
	Scandium (Sc) and Yttrium (Y) (typically considered in this		
	group though their atomic weight is lower)		

Table 20: C	lassification	of REEs u	under differe	nt groups
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Although REEs are relatively abundant, they are dispersed across ores in several geographies at very low concentrations, with only a few ores containing economically extractable REE reserves (USGS, 2022a; Zaimes et al., 2015). These ores are processed to first produce rare-earth oxides (or REOs), which are subsequently processed further to produce the final REEs. Given this chronology, REE production (at the mine level) is determined in REO-equivalent amounts or the amount of REO that can be produced from the quantity of material mined (USGS, 2022a).

In terms of REO-equivalent production, China has been the global leader for the last decade, accounting for 60% of production in 2021, with other significant producers being the United States (15%), Burma (9%), and Australia (8%) (USGS, 2022a). The lone ore source of REEs in the US is Mountain Pass, CA, which is operated on a care-and-maintenance mode (USGS, 2022a). However, the US Geological Survey data indicates that the US exports its REO-equivalent mined material production to China for further processing to REO and final REE (USGS, 2022a). Overall, the US has a > 90% import dependence for REEs and REE compounds, most of which are imported from China (USGS, 2022a). The US Geological Survey also shows a

similar production situation for scandium and yttrium to REEs, with the US being entirely import-dependent for the domestic needs of both these elements (USGS, 2022a). China, Russia, and the Philippines are major global scandium producers, while China and Burma dominate global yttrium production, with the predominant share of their imports to the US coming from China (USGS, 2022a).

5.2 REE Ore Sources

Globally, three types of ores dominate REE production: bastnäsite, monazite, and ionadsorption clays (Bailey et al., 2020; Vahidi et al., 2016; Vahidi and Zhao, 2017). Bastnäsite is a rare-earth fluoro-carbonate mineral, while monazite is a reddish-brown rare-earth phosphate mineral (Balaram, 2019). Ion-adsorption clays, better known as weathered clays, contain clay minerals like kaolin that contain REE ions (Vahidi et al., 2016). These ions are typically adsorbed from water that has dissolved REEs present in the parent rocks of clay formations such as granite (Vahidi et al., 2016). Such dissolution of rare-earth ions happens when two conditions are met: (a) Prolonged weathering of sedimentary rocks (containing REEs) that experience limited erosion; and (b) Presence of a clay crust with high aluminosilicate content that is capable of adsorbing REE ions (Vahidi et al., 2016).

As mentioned above, China dominates global REE production and is the biggest source of REE imports for the US. In China, REEs are extracted mainly in two regions: the Bayan Obo area in Inner Mongolia (that hosts a mix of bastnäsite and monazite ores), and Southern China (where the primary REE ore type is ion-adsorption clay) (Vahidi et al., 2016; Vahidi and Zhao, 2017). Within China's overall REO-equivalent mined mineral production, ~90% was obtained from the mix of bastnäsite and monazite reserves, with the remaining material obtained from ionadsorption clay ores. Although bastnäsite and monazite ores dominate the overall REE production, ion-adsorption clays are vital as they are needed to produce several heavy rare-earth elements (HREEs), as the content of these HREEs in bastnäsite and monazite reserves is negligible (Gupta et al., 2004; Schüler et al., 2011; Shi, 2009; Vahidi et al., 2016).

5.3 **REE Production Processes**

Given China's dominance in both REE production and the proportion of U.S.'s REE imports from China, we consider all production of final REE material, beginning with ore extraction, to be China-based processes. We acknowledge that about one-fifth of the United States' REE and REE compound imports come from other nations such as Japan, Estonia, and Malaysia (USGS, 2022a). However, it must be noted that even these nations process mineral concentrates from China and Australia for REE production (USGS, 2022a). Moreover, all processes described here for REE production are expected to also apply to similar minerals obtained from the other geographies.

The production of REEs from ores is a complex process undertaken across multiple steps. These steps can be grouped into two categories: (a) Production of rare-earth oxides (REOs) from the mined material/mineral; and (b) Production of REEs from REOs (Bailey et al., 2020; Vahidi et al., 2016; Vahidi and Zhao, 2018, 2017). We describe both these groups of processes in the sub-sections below.

5.3.1 Production of Rare Earth Oxides (REOs)

Production of REOs from ion-adsorption clays requires a very different set of processes compared to those needed for bastnäsite and monazite ores, at least until the leaching stage. The processes used for each ore type are described in the subsections below.

5.3.1.1 REO Production from Bastnäsite and Monazite Ores

Figure 6 shows a schematic of the process steps used for REO production from bastnäsite and monazite ores, while Figure 7 shows a detailed schematic of the solvent extraction step used for these ores (Vahidi and Zhao, 2017). A description of these schematics is given below.



Figure 6: Schematic of REO production from bastnäsite and monazite ores (reproduced using (Bailey et al., 2020; Vahidi et al., 2016; Vahidi and Zhao, 2018, 2017))



Figure 7: Schematic of solvent extraction of REOs (reproduced using (Bailey et al., 2020; Vahidi et al., 2016; Vahidi and Zhao, 2018, 2017))

China's Bayan Obo mine contains both bastnäsite and monazite reserves along with iron ores, all of which are extracted through open-pit mining (Bailey et al., 2020; Gupta and Krishnamurthy, 2016; Vahidi et al., 2016; Vahidi and Zhao, 2017). As Figure 6 shows, the ore is mined, crushed, and then treated with magnetic separation to remove iron content (Vahidi et al., 2016). The tailing (leftover material that contains REEs) is beneficiated via several conditioning treatments with steam and other reagents (such as fatty acids, sodium silicate, or hydroxomates like hydrogen peroxide) to obtain an REE concentrate with REO content of ~60% (Bailey et al., 2020; Gupta and Krishnamurthy, 2016; Vahidi et al., 2016). REE concentrate is roasted with sulfuric acid (H₂SO₄) at 550-650 °C, leaving behind REE precipitates as double sulfates (Bailey et al., 2020). These sulfates are leached using an acid-base reaction in two steps. First, REE double sulfates are reacted with dilute hydrochloric acid (HCl) and then subjected to alkaline treatment to selectively precipitate out the undesirable concentrates as residue (Bailey et al., 2020). Next, the useful sulfates are transformed into rare-earth chlorides (or RECIs) by reaction with concentrated HCl (Bailey et al., 2020). Note that the leachate (material obtained from the leaching process) is a mixture of various RECIs, and therefore, contains REE ions.

The most crucial step in REO production comes after leaching: solvent extraction – where the mix of REE ions is separated into individual REOs (Figure 7). A typical solvent extraction facility passes the leachate through multiple stages of mixer settlers (Vahidi and Zhao, 2017). Across these stages, the leachate is mixed with one of two organic extractants: P2O4 (Di-2-ethylhexyl phosphoric acid) or P5O7 (2-ethylhexyl phosphoric acid mono-2-ethylhexylester) (Bailey et al., 2020; Gupta and Krishnamurthy, 2016; Vahidi and Zhao, 2017). This blending causes REE ions (present in the aqueous phase) to move to the organic phase, where they can form more soluble REE compounds (Vahidi and Zhao, 2017). This is represented in the solvent

extraction facility's counterflow of organic and aqueous phases, where the aqueous phase moves from mixer settler *m* to m-1 simultaneously with the organic phase moving from mixer settler *m* to m+1 (Figure 7).

The loaded organic phase (containing REE ions) is then transferred for stripping, which completely reverses the reaction in mixer settlers of solvent extraction. Here, the organic phase is reacted with HCl, causing REE ions to transfer into a fresh aqueous medium due to their better solubility in this phase (Bailey et al., 2020; Vahidi and Zhao, 2017). This aqueous medium (also known as *strip liquor*) has an REE ion concentration nearly 10-100 times that in the leachate (Bailey et al., 2020). The stripped liquor is then reacted with either ammonium bicarbonate (NH₄HCO₃) or oxalic acid (C₂H₂O₄) to precipitate REE ions, which are calcined to obtain the concentrated, individual REOs (Gupta and Krishnamurthy, 2016; Vahidi and Zhao, 2017).

5.3.1.2 **REO Production from Ion-Adsorption Clays**

Compared to bastnäsite and monazite ores, REE extraction from ion-adsorption clays involves fewer steps, as shown in the schematic in Figure 8. The initial step is leaching, with several techniques available for this purpose, such as tank/pool, heap, and in-situ leaching (Schüler et al., 2011; Vahidi et al., 2016). The dominant leaching technology is in-situ leaching, as it requires less topsoil removal, has lower adverse environmental effects than other leaching methods, and can be conducted on the site of the ore (Schüler et al., 2011; Vahidi et al., 2016; Wu, 2005).

The actual in-situ leaching process involves a more complex setup. After selecting appropriate sites for mine exploration and injection wells throughout the site, an extensive pipeline network is built that consists of two major pipe systems (Vahidi et al., 2016; Yang et al., 2013). One system delivers ammonium sulfate ((NH₄)₂SO₄) as the leaching agent for ion-exchange reaction while also flushing water at the end of mining, while the other system is used to collect the leachate in pools (Vahidi et al., 2016; Zhu et al., 2013). Ion-adsorption clays are leached with ammonium sulfate over 150-400 days to produce leachate with high REE content for further processing. The residual REE-containing solution (with very low REO content) is flushed out by injecting freshwater (Vahidi et al., 2016; Zhu et al., 2013).

Leachate (from in-situ leaching) is purified using impurity-removing agents and is then reacted with either ammonium bicarbonate (NH₄HCO₃) or oxalic acid (C₂H₂O₄) to precipitate the REE ions (Vahidi et al., 2016). While ammonium bicarbonate is preferred for its lower costs and reduced environmental impacts, oxalic acid can deliver higher purity product and help avoid challenges in the subsequent dehydration step that are seen upon using ammonium bicarbonate (Chi et al., 2003; Vahidi et al., 2016). In either case, the precipitates are dehydrated to remove water, filtered, mechanically pressed, and calcined at 750-850°C to obtain REOs with 90-92% purity (Bailey et al., 2020; Schüler et al., 2011; Vahidi et al., 2016). The obtained REOs are purified further using solvent extraction – similar to the solvent extraction process used for REO production from bastnäsite and monazite ores (Bailey et al., 2020). However, unlike for bastnäsite and monazite ores, the solvent extraction process here requires sodium hydroxide for converting intermediate RECls to REOs (Bailey et al., 2020).



Figure 8: Schematic of REO production from ion-adsorption clays

5.3.2 Production of Rare Earth Elements (REEs)

Regardless of the ore type, solvent extraction leads to the obtainment of separate, individual REOs. However, the strong affinity of REEs to oxygen makes the breakdown of REEs a challenging task (Vahidi and Zhao, 2018). The typical technique used to produce REEs from REOs is molten salt electrolysis (MSE), where the REOs are converted to rare-earth halides (usually rare-earth fluorides or REFs) and then reduced to REEs (Vahidi and Zhao, 2018). MSE has been reported to be effective in producing some REEs, such as lanthanum, cerium, praseodymium, and neodymium, from their respective REOs (Lee and Wen, 2017). However, other types of reduction methods, such as calciothermic and metallothermic reduction, have also been indicated as being usable for other REEs like gadolinium, holmium, samarium, and ytterbium (Vahidi and Zhao, 2018)

Figure 9 shows the general schematic of the process flow used to produce REEs from REOs, (Vahidi and Zhao, 2018). Initially, rare-earth fluorides (REFs) are produced by passing dry hydrogen fluoride (HF) gas via a sealed tube of nickel alloy and reacting it with REOs at 550-650°C in an electric fluoride furnace. To achieve higher reaction efficiencies and minimal loss of HF, a water spray absorption system is used to convert waste HF into hydrofluoric acid (20%) solution. The REFs obtained from this process are combined with lithium fluoride (LiF) in an 85:15 ratio, and the blend is mixed with REOs – it is this mixture (REO/LiF/REF) that is used

in a molten state as the MSE electrolyte. While LiF both reduces the melting point of the electrolyte and enhances its conductivity, REFs help improve the solubility of REOs in the electrolyte. The MSE cell also employs cathodes made from tantalum, tungsten, or molybdenum (molybdenum is the most used among these), and graphitic anodes. REE ions reduce to metallic REE at the cathode, while oxygen ions oxidize and react with a graphite anode to produce CO and CO₂.



Figure 9: Schematic of REE production from REO

5.4 REE Production: Material and Energy Flows

Life-cycle analysis (LCA) of REE production has been conducted in multiple studies over the past ten years. All these studies provide material and energy flow details for producing REO/REE from one of the three ore types (bastnäsite, monazite, and ion-adsorption), with most studies based on China. Table 21 lists these studies, including their geography of focus, their system boundary, and ore type.

Ref.	Geographical scope	System boundary	Ore type
(Navarro and Zhao, 2014)	China and US	Ore to REO	Bastnäsite/Monazite Ion-adsorption clays
(Nuss et al., 2014)	Global	Ore to REO	Bastnäsite
(Sprecher et al., 2014)	China	Ores to Neodymium Oxide	Bastnäsite/Monazite
(Zaimes et al., 2015)	China	Ore to REO	Bastnäsite/Monazite
(Jin et al., 2016)	China	Recycled Nd-Fe-B magnet	Not applicable
(Schreiber et al., 2016)	Norway	Ore to Neodymium or Dysprosium	Eudialyte and Bastnäsite
(Vahidi et al., 2016)	China	Ore to REO	Ion-adsorption clay
(Weng et al., 2016)	China	Ore to REO	Bastnäsite/Monazite Ion-adsorption clays
(Ikhlayel, 2017)	China	Ore to REE	Unclear
(Lee and Wen, 2017)	China	Ore to REE	Bastnäsite
(Schulze et al., 2017)	China	Ore to REO	Ion-adsorption clay
(Vahidi and Zhao, 2017)	China	Ore to REO	Bastnäsite/Monazite
(Vahidi and Zhao, 2018)	China	REO to REE	REOs from all ore types
(Bailey et al., 2020)	China	Ore to REO	Bastnäsite/Monazite Ion-adsorption clays

 Table 21: A summary of studies that provide material and energy flow details for producing REOs and/or REEs

As we have already mentioned, REEs are produced by initially producing REOs from mined ore and processing them further to the pure element form. For REO production from all ore types, we use material and energy flows from Bailey et al. (2020) in the updated GREET model, as it provides the most recent and the most comprehensive data on these flows. For the same reasons, we use the material and energy flows from Vahidi and Zhao (2018) for processes used to produce REEs from REOs. Table 22 provides the material and energy flows for REO production from ores for all ore types. Table 23 provides these flows for REF production, while Table 24 shows these flows for REE production from REOs.

Since REOs are produced together, the environmental impacts of REO production are allocated across different REOs. In the updated GREET model, we use mass allocation based on mass content (wt.%) of REO in the ore types (bastnäsite/monazite, ion-adsorption). Table 25 shows the mass allocation shares used for REOs produced from both types of ores.

All the material and energy flows for REO and REE production, as well as the associated life-cycle energy use and emission calculations, are shown in the Rare_Earth sheet of the updated GREET2 2022 model.

Table 22: Material and Energy Flows for REO Production

		Production from	Production from Ion- Adsorption Clays				
Materials/Energy Sources	Mining	Beneficiation	Acid Roasting	Leaching	Solvent Extraction	Mining	Solvent Extraction
Material inputs (ton/ton of pr	ocess outpu	it)		· · ·		·	
Ammonium nitrate	0.0005						
Water	3.400	17.4		8.260	204.200	1,000	59.896
Sodium silicate		0.068					
Hydrogen pentoxide		0.032					
Ammonium hydroxide		0.047					
Sulfuric acid			1.55			0.525	
Sulfidic tailings disposal			0.505				
Sodium carbonate/Soda ash				1	1.05		
Hydrochloric acid				0.2	1 0		0.060
(30% in solution)				0.5	1.0		0.909
P2O4					0.005		0.025
Ammonia					0.6		
Kerosene					0.02		
Ammonium bicarbonate					1.6	3.35	
Graphite					0.041		
Polyvinylchloride						0.095	
Limestone/Calcium carbonate						0.005	
Ammonium sulfate						8.25	
Extruded pipe (PVC)						0.101	
Spent solvent mixture							$1.05 imes 10^{-5}$
Sodium hydroxide							1 225
(50% in solution)							1.555
Citric acid							0.791
Energy inputs (mmBtu/ton of	process ou	tput)					
Residual oil			5.662				
Diesel	1.074						
Electricity		1.030			18.558	9.625	0.820

Table 22 (Cont.)

Materials/Energy Sources		Production fro	Production from Ion- Adsorption Clays									
	Mining	Beneficiation	Acid Roasting	Leaching	Solvent Extraction	Mining	Solvent Extraction					
Emission outputs (g/ton of process output)												
VOC												
СО												
NO _x							2,113.74					
PM_{10}	1,179.34											
PM _{2.5}	130.635											
SO _x			8,264.453				14.606					
BC												
OC												
CH_4												
N ₂ O					6,095.306							
CO ₂			139,706		1,312,289	417,305	921					

Table 23: Material and Energy Flows for Rare Earth Fluoride (REF) Production

Materials/Energy	Praseodymium	Neodymium-Praseodymium	Gadolinium	Dysprosium						
Sources	fluoride	fluoride	fluoride	fluoride						
Material inputs (ton/ton of process output)										
Water	1.51	1.53	1.51	1.51						
Hydrogen fluoride	0.331	0.336	0.331	0.331						
Praseodymium oxide	0.755	0.189								
Neodymium oxide		0.566								
Gadolinium oxide			0.755							
Dysprosium oxide				0.755						
Energy inputs (ton/ton of p	rocess output)									
Electricity	0.002	0.001	0.001	0.006						

Materials/Energy	Praseodymium			Neodymium			thanum	Tarbium	Samanium	
Sources	Source 1	Source 2	Source 1	Source 2	Source 3	Source 1	Source 2	Terblum	Samarium	
Water	51.7	3.9	12.9	12.6	12.1	1.03	0.959	123	4.91	
Graphite	0.223	0.051	0.17	0.26	0.113	0.021	$8.94 imes10^{-6}$	0.011	4.58×10^{-5}	
Lime								0.821		
Praseodymium oxide	1.17	1.18								
Neodymium oxide			1.15	1.15	1.16					
Lithium fluoride	0.0096	0.0019	0.0062	0.013	0.004	0.0011	$3.18 imes 10^{-7}$	4.07×10^{-5}	$1.63 imes 10^{-6}$	
Molybdenum	0.00036	$8.68 imes10^{-5}$	$2.88 imes 10^{-4}$	0.0013	0.0007	$1.07 imes 10^{-4}$	$5.70 imes10^{-8}$	$7.30 imes 10^{-6}$	$2.92 imes 10^{-7}$	
Steel	0.0036	0.0009	0.0029		0.035		$2.78 imes10^{-6}$	3.55×10^{-4}	1.42×10^{-5}	
Alumina (Refractory)	0.033	0.0072	0.024		1.58×10^{-4}		$1.25 imes 10^{-8}$	1.60×10^{-6}	$6.40 imes 10^{-8}$	
Praseodymium fluoride	0.08	0.07								
Neodymium- Praseodymium fluoride			0.07	0.08	0.049	0.1	0.041	0.05	0.05	
Lanthanum oxide						1.16	1.62			
Terbium oxide								1.4		
Argon					0.015	1.03	$1.20 imes 10^{-6}$	1.53×10^{-4}	6.13×10^{-6}	
Samarium oxide									1.18	
Lanthanum									0.920	
Energy inputs (ton/to	on of proces	s output)								
Electricity	0.034	0.058	0.032	0.039	0.021	0.003	0.002	0.218	0.009	

 Table 24: Material and Energy Flows for Rare Earth Element (REE) Production

Table 24 (Cont.)

Materials/Energy	Praseodymium		Ν	Neodymium			thanum	Terbium	Samarium
Sources	Source 1	Source 2	Source 1	Source 2	Source 3	Source 1	Source 2		
Emissions (ton/ton of p	Emissions (ton/ton of process output)								
VOC									
СО	304,814								
NO _x									
PM_{10}	2,087	18.053	59.965	1,551	403	127	0.032	4.082	0.163
PM _{2.5}	9.072	821	2,722						
SO _x									
BC									
OC									
CH_4									
N ₂ O									
CO ₂	100,698								

REOs	Bastnäsite/Monazite	Ion-adsorption clays
Lanthanum oxide (La ₂ O ₃)	23.9%	28.0%
Cerium oxide (Ce ₂ O ₃)	50.3%	3.3%
Praseodymium oxide (Pr ₆ O ₁₁)	5.8%	5.7%
Neodymium oxide (Nd ₂ O ₃)	17.9%	17.9%
Samarium oxide (Sm ₂ O ₃)	0.9%	4.6%
Europium oxide (Eu ₂ O ₃)	0.2%	0.9%
Gadolinium oxide (Gd ₂ O ₃)	0.7%	6.0%
Terbium oxide (Tb ₄ O ₇)	0.1%	0.7%
Dysprosium oxide (Dy ₂ O ₃)	0.1%	3.8%
Holmium oxide (Ho ₂ O ₃)	0.0%	0.5%
Erbium oxide (Er ₂ O ₃)	0.0%	2.5%
Thulium oxide (Tm ₂ O ₃)	0.0%	0.5%
Ytterbium oxide (Yb ₂ O ₃)	0.0%	0.5%
Lutetium oxide (Lu ₂ O ₃)	0.0%	0.5%
Yttrium oxide (Y ₂ O ₃)	0.1%	24.6%

Table 25: Mass content (allocation ratios) for various ore types

5.5 REE-Based Materials and Components: Material and Energy Flows

The GREET model provides the material composition and weights of both vehicles (light-, medium-, and heavy-duty) and their constituent component systems (such as body, powertrain, transmission, and batteries) across different powertrains. Traction motors are a key component of vehicles with hybrid, electric, and fuel-cell powertrains, with magnets being one of their essential constituents. These magnets are typically Nd(Dy)FeB or neodymium-iron-boron magnets that also contain some dysprosium. We have combined the material and energy flow data from Nordelöf and Tillman (2018) with our inventory (energy use and emission calculations) for REEs (Nd and Dy) to determine the material and energy flow data and resultant energy use and emissions for magnet production. These flows are shown in the Rare Earth sheet of the updated GREET model (GREET2), and the obtained energy use and emissions are subsequently used in calculations of vehicle-cycle and life-cycle energy use and emissions of different vehicles. Table 26 shows the material and energy flows for magnet production. Apart from magnets, Ni-MH (nickel-metal hydride) batteries are another component system that use REEs. Based on the material composition of rare-earths used in these batteries - reported in Meshram et al. (2016) and shown in Table 27, we have updated the inventory (energy use and emission) calculations for REE mix used in Ni-MH batteries in the Rare Earth sheet of updated GREET (GREET2).

Materials/Energy Sources	Nd(Dy) FeB Magnet
Material inputs (ton/ton of magnet)	
Water	6.0
Sulfuric acid	0.0014
Sodium hydroxide (50% in solution)	0.001
Hydrogen	0.6
Dysprosium oxide	0.091
Iron	0.83
Boron carbide	0.015
Neodymium	0.31
Nickel	0.011
Energy inputs (mmBtu/ton of magnet)	
Electricity	43.303

Table 26: Material and energy flows of Nd(Dy)FeB magnet production

Table 27: REE mix used in Ni-MH batteries

REEs	Wt.% within REEs used in Ni-MH batteries (wt.%)
Lanthanum (La)	17.2
Neodymium (Nd)	28.7
Samarium (Sm)	39.5
Praseodymium (Pr)	14.6

6 INTERMEDIATE MATERIALS: MATERIAL AND ENERGY FLOWS

6.1 Sodium Silicate

Apart from its considerable abundance, silicon (Si) is also known to form a long list of important compounds, next only to carbon (Martha et al., 2022). Silicates comprise a crucial chunk of these compounds, found both in natural forms and also produced in mass quantities (Fawer et al., 1999; Liu and Ott, 2020). Sodium silicate (SS) is considered among the most significant silicates due to its favorable properties, such as its non-toxicity, non-flammable and non-explosive nature, low costs, and its recognition as an environment-friendly substance (Liu and Ott, 2020). These properties enable SS to be used extensively over a diverse range of sectors, including in adhesives, binders, cleaning compounds, corrosion inhibitors, catalyst bases, coatings, detergents, and in geothermal well applications (like drilling and integrity repair of casing wells) (Liu and Ott, 2020). Here, SS is used in the beneficiation process for REO production from bastnäsite and monazite ores (Bailey et al., 2020), and is thus, an input flow for this process in the updated GREET[®] model.



Figure 10: Schematic of production of sodium silicate (SS)

Figure 10 shows the schematic for the production of SS powders (Fawer et al., 1999). Silica sand is hydrothermally dissolved in sodium hydroxide solution in autoclaves that can withstand the extreme operating conditions used for this step. The product from this step (SS solution, 48% solid) is spray-dried to yield SS hydrous powders (with 20% water content). These powders are used in the beneficiation process for REO production (Bailey et al., 2020). Table 28 provides the material and energy flows for SS production (Fawer et al., 1999).

Material/Energy Source	Value
Material inputs (ton/ton of sodium silicate spray powde	r)
Rock salt	0.214
Sand	0.562
Limestone	0.0038
Water	815.30
Additives	0.0016
Energy inputs (ton/ton of sodium silicate spray powder)	
Electricity	6.474
Coal	0.473
Residual oil	0.733
Diesel	0.193
Natural gas	7.586
Emissions (ton/ton of sodium silicate spray powder)	
VOC	2,348
СО	462
NO _X	3,166
SO ₂	3,793
CH ₄	1,214
CO ₂	809,529

 Table 28: Material and energy flows for sodium silicate production (Fawer et al., 1999)

6.2 Ozone (O₃)

Ozone is an oxidant mainly used for drinking water and wastewater treatment as it is highly capable of oxidizing multiple organic pollutants (Da Silva et al., 2010; Magara et al., 1995). Ozonation is typically used to treat water for several industries, such as pharmaceuticals, wood pulp bleaching, and textiles (Da Silva et al., 2010; Franco et al., 2008). Ozone is commercially produced by discharging oxygen (O_2) and/or O_2 -containing gas passed between two electrodes separated by a dielectric (Da Silva et al., 2010; Franco et al., 2008; Magara et al., 1995). The actual reaction involves a collision between the electrons and O_2 molecules, with ozone formed via a reaction between O_2 molecules and O atoms (or excited and normal O_2 molecules) in the presence of a catalyst. Dehumidifiers and cooling units are used to reduce moisture and achieve high ozone production efficiency (Magara et al., 1995). Table 29 shows the material and energy flows for ozone production (Magara et al., 1995).

Table	29.	Material	and	energy	flows	for	070De	nroduction	(Ma	oara (at al	1995)
Table	49:	Material	anu	energy	nows	IOL	ozone	production	(1114	gara e	et al.,	, 1993	J

Material/Energy Source	Value					
Material inputs (ton/ton of ozone produced)						
Oxygen	1.00					
Energy inputs (ton/ton of ozone produced)						
Electricity	24.744					

6.3 Hydrogen Pentoxide (H₂O₅)

Hydrogen pentoxide (H_2O_5) is produced via a chemical reaction between ozone (O_3) and hydrogen peroxide (H_2O_2) (Tizaoui et al., 2007). More details on this chemical remain unavailable, so no energy inputs are considered in its production. Table 30 shows the material flows for H_2O_5 production based on mass stoichiometry.

Table 30: Material and energy flows f	or hydrogen pentoxide production
---------------------------------------	----------------------------------

Material	Value		
Material inputs (ton/ton of hydrogen pentoxide produced)			
Ozone	0.585		
Hydrogen peroxide	0.415		

6.4 P204

Di-2-ethylhexyl phosphoric acid, or P204, is a commonly used organic extractant (Vahidi and Zhao, 2017). It is primarily used in the hydrometallurgical separation/production of copper, cobalt, nickel, and REEs (Vahidi and Zhao, 2017). Figure 11 shows the schematic for P204 production, with its brief description given below (Vahidi and Zhao, 2017).



Figure 11: Schematic of production of P204 (di-2-ethylhexyl phosphoric acid) (Vahidi and Zhao, 2017)

First, synthesis gas (CO + H₂ gas) is reacted with propylene to produce normal butyraldehyde. Next, n-butyraldehyde molecules are reacted via aldolization to produce butyraldol, that is converted to 2-ethyl 3-propyl acrolein (EPA) by dehydration reaction in the presence of aqueous caustic soda at 120°C. EPA is then hydrogenated at ~160°C and 30 bar to produce 2-ethylhexanol as a byproduct, which is reacted with phosphorus trichloride (PCl₃) in an esterification reaction under inert atmosphere at 10-15°C. Chlorine is then added to the mixture at 20°C over 2-3 hours to produce phosphochloridate through oxidizing diphosphite. Finally, hydrolysis is conducted at 80-100°C for 2 h over-and-beyond the stoichiometric amount to produce P204. Table 31 shows the material and energy flows for the production of P204.

Material/Energy Source	Value				
Material inputs (ton/ton of P204 produced)					
Water	0.362				
Sodium hydroxide (50% in solution)	0.166				
Carbon monoxide	1.03				
Phosphorus trichloride	0.616				
Propylene	0.286				
Hydrogen	1.55				
Nitrogen	0.273				
Energy inputs (ton/ton of P204 produced)					
Electricity	0.773				

Table 31: Material and energy flows for P204 production

6.5 Ammonium bicarbonate (NH4HCO3)

Ammonium bicarbonate is obtained through an endothermic reaction of water (H₂O), ammonia (NH₃), and carbon dioxide (CO₂) (Althaus et al., 2007). Table 32 lists the material and energy flows of NH₄HCO₃ production (Althaus et al., 2007).

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Tabla	27.	Matarial	and	OBORGE	flow	for	ommonium	hioon	honoto	nnoduction
rame.	54:	wateria	anu	energy	nows	IOF	ammonnum	DICAL	Donate	Drouuction

Material/Energy Source	Value				
Material inputs (ton/ton of material produced)					
Water	0.24				
Ammonia	0.227				
Carbon dioxide	0.586				
Energy inputs (ton/ton of material produced)					
Electricity	0.999				

REFERENCES

- Althaus, H.-J., Hischier, R., Osses, M., Primas, A., Hellweg, S., Jungbluth, N., Chudacoff, M., Chudacoff, Ö., 2007. Life Cycle Inventories of Chemicals Data v2.0 (2007). Zurich.
- Babbitt, C.W., Althaf, S., Cruz Rios, F., Bilec, M.M., Graedel, T.E., 2021. The role of design in circular economy solutions for critical materials. One Earth 4, 353–362. https://doi.org/10.1016/J.ONEEAR.2021.02.014
- Bailey, G., Joyce, P.J., Schrijvers, D., Schulze, R., Sylvestre, A.M., Sprecher, B., Vahidi, E., Dewulf, W., Van Acker, K., 2020. Review and new life cycle assessment for rare earth production from bastnäsite, ion adsorption clays and lateritic monazite. Resour. Conserv. Recycl. 155, 104675. https://doi.org/10.1016/J.RESCONREC.2019.104675
- Balaram, V., 2019. Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. Geosci. Front. 10, 1285–1303. https://doi.org/10.1016/J.GSF.2018.12.005
- Benavides, P.T., Dai, Q., Sullivan, J.L., Kelly, J.C., Dunn, J.B., 2015. Material and Energy Flows Associated with Select Metals in GREET 2. Molybdenum, Platinum, Zinc, Nickel, Silicon (No. ANL/ESD-15/11). Argonne, IL (United States). https://doi.org/10.2172/1224976
- Brinson, A., Gioia, M. De, Tanudisastro, G.F., Jimenez, M.L., Djohari, J.T., Sykes, C., 2020. Zero Emission Copper Mine of the Future.
- Chen, J., Wang, Z., Wu, Y., Li, L., Li, B., Pan, D., Zuo, T., 2019. Environmental benefits of secondary copper from primary copper based on life cycle assessment in China. Resour. Conserv. Recycl. 146, 35–44. https://doi.org/10.1016/J.RESCONREC.2019.03.020
- Chi, R., Zhou, Z., Xu, Z., Hu, Y., Zhu, G., Xu, S., 2003. Solution-chemistry analysis of ammonium bicarbonate consumption in rare-earth-element precipitation. Metall. Mater. Trans. B 34, 611–617. https://doi.org/10.1007/s11663-003-0031-z
- Da Silva, L.M., Franco, D. V., Sousa, L.G., Gonçalves, I.C., 2010. Characterization of an electrochemical reactor for the ozone production in electrolyte-free water. J. Appl. Electrochem. 40, 855–864. https://doi.org/10.1007/S10800-009-0069-Y/FIGURES/11
- Deng, S.Y., Gong, X.Z., 2018. Life Cycle Assessment of Nickel Production in China. Mater. Sci. Forum 913, 1004–1010. https://doi.org/10.4028/WWW.SCIENTIFIC.NET/MSF.913.1004
- Dong, D., van Oers, L., Tukker, A., van der Voet, E., 2020. Assessing the future environmental impacts of copper production in China: Implications of the energy transition. J. Clean. Prod. 274, 122825. https://doi.org/10.1016/J.JCLEPRO.2020.122825

- Elshkaki, A., Reck, B.K., Graedel, T.E., 2017. Anthropogenic nickel supply, demand, and associated energy and water use. Resour. Conserv. Recycl. 125, 300–307. https://doi.org/10.1016/J.RESCONREC.2017.07.002
- Evans, P., 2015. Density of Gases [WWW Document]. Eng. Mindset. URL https://theengineeringmindset.com/density-of-gases/ (accessed 10.19.22).
- Fawer, M., Concannon, M., Rieber, W., 1999. Life cycle inventories for the production of sodium silicates. Int. J. Life Cycle Assess. 1999 44 4, 207–212. https://doi.org/10.1007/BF02979498
- Franco, D. V., Jardim, W.F., Boodts, J.F.C., Da Silva, L.M., 2008. Electrochemical Ozone Production as an Environmentally Friendly Technology for Water Treatment. CLEAN – Soil, Air, Water 36, 34–44. https://doi.org/10.1002/CLEN.200700080
- Free, M.L., 2020. A brief introduction to production of titanium dioxide and titanium tetrachloride, in: Fang, Z.Z., Froes, F.H., Zhang, Y. (Eds.), Extractive Metallurgy of Titanium: Conventional and Recent Advances in Extraction and Production of Titanium Metal. Elsevier, pp. 13–18. https://doi.org/10.1016/B978-0-12-817200-1.00002-8
- Fthenakis, V., Wang, W., Kim, H.C., 2009. Life cycle inventory analysis of the production of metals used in photovoltaics. Renew. Sustain. Energy Rev. 13, 493–517. https://doi.org/10.1016/J.RSER.2007.11.012
- Gao, F., Nie, Z., Yang, D., Sun, B., Liu, Y., Gong, X., Wang, Z., 2018. Environmental impacts analysis of titanium sponge production using Kroll process in China. J. Clean. Prod. 174, 771–779. https://doi.org/10.1016/J.JCLEPRO.2017.09.240
- Gaustad, G., Krystofik, M., Bustamante, M., Badami, K., 2018. Circular economy strategies for mitigating critical material supply issues. Resour. Conserv. Recycl. 135, 24–33. https://doi.org/10.1016/J.RESCONREC.2017.08.002
- Guohua, Y., Elshkaki, A., Xiao, X., 2021. Dynamic analysis of future nickel demand, supply, and associated materials, energy, water, and carbon emissions in China. Resour. Policy 74, 102432. https://doi.org/10.1016/J.RESOURPOL.2021.102432
- Gupta, C.K., Krishnamurthy, N., 2016. Extractive Metallurgy of Rare Earths, 2md ed. Taylor & Francis Group, Boca Raton.
- Gupta, G.K., Krishnamurthy, N., Gupta, C.K., Krishnamurthy, N., 2004. Extractive Metallurgy of Rare Earths, 1st ed, https://doi.org/10.1179/imr.1992.37.1.197. CRC Press, Boca Raton. https://doi.org/10.1179/IMR.1992.37.1.197
- Henckens, M.L.C.M., Worrell, E., 2020. Reviewing the availability of copper and nickel for future generations. The balance between production growth, sustainability and recycling rates. J. Clean. Prod. 264, 121460. https://doi.org/10.1016/J.JCLEPRO.2020.121460

- Ikhlayel, M., 2017. Evaluation of the environmental impacts of rare earth elements production. http://dx.doi.org/10.1080/00207233.2017.1341737 74, 939–957. https://doi.org/10.1080/00207233.2017.1341737
- Jin, H., Afiuny, P., McIntyre, T., Yih, Y., Sutherland, J.W., 2016. Comparative Life Cycle Assessment of NdFeB Magnets: Virgin Production versus Magnet-to-Magnet Recycling. Procedia CIRP 48, 45–50. https://doi.org/10.1016/J.PROCIR.2016.03.013
- Kelly, J.C., Dai, Q., Wang, M., 2019. Globally regional life cycle analysis of automotive lithiumion nickel manganese cobalt batteries. Mitig. Adapt. Strateg. Glob. Chang. 2019 253 25, 371–396. https://doi.org/10.1007/S11027-019-09869-2
- Kerfoot, D.E.G., 2000. Nickel, in: Weinhelim: VCH Verlag (Ed.), Ullmann's Encyclopedia of Industrial Chemistry. John Wiley & Sons, Ltd, Weinheim, Germany, pp. 158–219. https://doi.org/10.1002/14356007.A17_157
- Khoo, J.Z., Haque, N., Bhattacharya, S., 2017a. Process simulation and exergy analysis of two nickel laterite processing technologies. Int. J. Miner. Process. 161, 83–93. https://doi.org/10.1016/J.MINPRO.2017.02.012
- Khoo, J.Z., Haque, N., Woodbridge, G., McDonald, R., Bhattacharya, S., 2017b. A life cycle assessment of a new laterite processing technology. J. Clean. Prod. 142, 1765–1777. https://doi.org/10.1016/J.JCLEPRO.2016.11.111
- Koppelaar, R.H.E.M., Koppelaar, H., 2016. The Ore Grade and Depth Influence on Copper Energy Inputs. Biophys. Econ. Resour. Qual. 1, 1–16. https://doi.org/10.1007/S41247-016-0012-X
- Kuipers, K.J.J., van Oers, L.F.C.M., Verboon, M., van der Voet, E., 2018. Assessing environmental implications associated with global copper demand and supply scenarios from 2010 to 2050. Glob. Environ. Chang. 49, 106–115. https://doi.org/10.1016/J.GLOENVCHA.2018.02.008
- Kulczycka, J., Lelek, Ł., Lewandowska, A., Wirth, H., Bergesen, J.D., 2016. Environmental Impacts of Energy-Efficient Pyrometallurgical Copper Smelting Technologies: The Consequences of Technological Changes from 2010 to 2050. J. Ind. Ecol. 20, 304–316. https://doi.org/10.1111/JIEC.12369
- Lee, J.C.K., Wen, Z., 2017. Rare Earths from Mines to Metals: Comparing Environmental Impacts from China's Main Production Pathways. J. Ind. Ecol. 21, 1277–1290.
- Liu, S., Ott, W.K., 2020. Sodium silicate applications in oil, gas & geothermal well operations. J. Pet. Sci. Eng. 195, 107693. https://doi.org/10.1016/J.PETROL.2020.107693
- Lossin, A., 2001. Copper, in: Ullmann, F. (Ed.), Ullmann's Encyclopedia of Industrial Chemistry. John Wiley & Sons, Ltd, Weinheim, Germany, pp. 163–227. https://doi.org/10.1002/14356007.A07_471

- Magara, Y., Itoh, M., Morioka, T., 1995. Application of ozone to water treatment and power consumption of ozone generating systems. Prog. Nucl. Energy 29, 175–182. https://doi.org/10.1016/0149-1970(95)00041-H
- Martha, S.K., Elias, L., Ghosh, S., 2022. Nanostructured 3D (three dimensional) electrode architectures of silicon for high-performance Li-ion batteries. Silicon Anode Syst. Lithium-Ion Batter. 331–371. https://doi.org/10.1016/B978-0-12-819660-1.00013-X
- Meshram, P., Pandey, B.D., Mankhand, T.R., 2016. Process optimization and kinetics for leaching of rare earth metals from the spent Ni–metal hydride batteries. Waste Manag. 51, 196–203. https://doi.org/10.1016/J.WASMAN.2015.12.018
- Middlemas, S., Fang, Z.Z., Fan, P., 2015. Life cycle assessment comparison of emerging and traditional Titanium dioxide manufacturing processes. J. Clean. Prod. 89, 137–147. https://doi.org/10.1016/J.JCLEPRO.2014.11.019
- Moreau, K., Laamanen, C., Bose, R., Shang, H., Scott, J.A., 2021. Environmental impact improvements due to introducing automation into underground copper mines. Int. J. Min. Sci. Technol. 31, 1159–1167. https://doi.org/10.1016/J.IJMST.2021.11.009
- Mudd, G.M., 2010. Global trends and environmental issues in nickel mining: Sulfides versus laterites. Ore Geol. Rev. 38, 9–26. https://doi.org/10.1016/J.OREGEOREV.2010.05.003
- Mudd, G.M., Jowitt, S.M., 2014. A Detailed Assessment of Global Nickel Resource Trends and Endowments. Econ. Geol. 109, 1813–1841. https://doi.org/10.2113/ECONGEO.109.7.1813
- Mudd, G.M., Weng, Z., Jowitt, S.M., 2013. A Detailed Assessment of Global Cu Resource Trends and Endowments. Econ. Geol. 108, 1163–1183. https://doi.org/10.2113/ECONGEO.108.5.1163
- Navarro, J., Zhao, F., 2014. Life-cycle assessment of the production of rare-earth elements for energy applications: A review. Front. Energy Res. 2, 45. https://doi.org/10.3389/FENRG.2014.00045/BIBTEX
- Nordelöf, A., Tillman, A.M., 2018. A scalable life cycle inventory of an electrical automotive traction machine—Part II: manufacturing processes. Int. J. Life Cycle Assess. 23, 295–313. https://doi.org/10.1007/S11367-017-1309-8/FIGURES/5
- Norgate, T., Haque, N., 2010. Energy and greenhouse gas impacts of mining and mineral processing operations. J. Clean. Prod. 18, 266–274. https://doi.org/10.1016/j.jclepro.2009.09.020
- Norgate, T., Jahanshahi, S., 2011. Assessing the energy and greenhouse gas footprints of nickel laterite processing. Miner. Eng. 24, 698–707. https://doi.org/10.1016/J.MINENG.2010.10.002
- Norgate, T., Jahanshahi, S., 2010. Low grade ores Smelt, leach or concentrate? Miner. Eng. 23, 65–73. https://doi.org/10.1016/J.MINENG.2009.10.002

- Northey, S., Haque, N., Mudd, G., 2013. Using sustainability reporting to assess the environmental footprint of copper mining. J. Clean. Prod. 40, 118–128. https://doi.org/10.1016/J.JCLEPRO.2012.09.027
- Northey, S., Mohr, S., Mudd, G.M., Weng, Z., Giurco, D., 2014. Modelling future copper ore grade decline based on a detailed assessment of copper resources and mining. Resour. Conserv. Recycl. 83, 190–201. https://doi.org/10.1016/J.RESCONREC.2013.10.005
- Northey, S.A., Haque, N., Lovel, R., Cooksey, M.A., 2014. Evaluating the application of water footprint methods to primary metal production systems. Miner. Eng. 69, 65–80. https://doi.org/10.1016/J.MINENG.2014.07.006
- Nuss, P., Eckelman, M.J., Yamaguchi, H., Inaba, A., Friedlander, E., 2014. Life Cycle Assessment of Metals: A Scientific Synthesis. PLoS One 9, e101298. https://doi.org/10.1371/journal.pone.0101298
- Perks, C., Mudd, G., 2019. Titanium, zirconium resources and production: A state of the art literature review. Ore Geol. Rev. 107, 629–646. https://doi.org/10.1016/J.OREGEOREV.2019.02.025
- Sanjuan-Delmás, D., Alvarenga, R.A.F., Lindblom, M., Kampmann, T.C., van Oers, L., Guinée, J.B., Dewulf, J., 2022. Environmental assessment of copper production in Europe: an LCA case study from Sweden conducted using two conventional software-database setups. Int. J. Life Cycle Assess. 27, 255–266. https://doi.org/10.1007/S11367-021-02018-5/TABLES/5
- Schreiber, A., Marx, J., Zapp, P., Hake, J.F., Voßenkaul, D., Friedrich, B., 2016. Environmental Impacts of Rare Earth Mining and Separation Based on Eudialyte: A New European Way. Resour. 2016, Vol. 5, Page 32 5, 32. https://doi.org/10.3390/RESOURCES5040032
- Schüler, D., Buchert, M., Liu, R., Dittrich, S., Merz, C., 2011. Study on Rare Earths and their Recycling. Darmstadt.
- Schulze, R., Lartigue-Peyrou, F., Ding, J., Schebek, L., Buchert, M., 2017. Developing a Life Cycle Inventory for Rare Earth Oxides from Ion-Adsorption Deposits: Key Impacts and Further Research Needs. J. Sustain. Metall. 2017 34 3, 753–771. https://doi.org/10.1007/S40831-017-0139-Z
- Serres, N., Tidu, D., Sankare, S., Hlawka, F., 2011. Environmental comparison of MESO-CLAD® process and conventional machining implementing life cycle assessment. J. Clean. Prod. 19, 1117–1124. https://doi.org/10.1016/J.JCLEPRO.2010.12.010
- Shi, F., 2009. Rare earth metallurgy technology. Publisher of Metallurgical Industry, Beijing.
- Sibum, H., Güther, V., Roidl, O., Habashi, F., Wolf, H.U., Siemers, C., 2017. Titanium, Titanium Alloys, and Titanium Compounds, in: Ullmann's Encyclopedia of Industrial Chemistry. John Wiley & Sons, Ltd, pp. 1–35. https://doi.org/10.1002/14356007.A27_095.PUB2

Sphera, 2020. Life Cycle Assessment of Nickel Products.

- Sprecher, B., Xiao, Y., Walton, A., Speight, J., Harris, R., Kleijn, R., Visser, G., Kramer, G.J., 2014. Life cycle inventory of the production of rare earths and the subsequent production of NdFeB rare earth permanent magnets. Environ. Sci. Technol. 48, 3951–3958. https://doi.org/10.1021/ES404596Q/SUPPL_FILE/ES404596Q_SI_002.XLSX
- Sverdrup, H.U., Ragnarsdottir, K.V., Koca, D., 2014. On modelling the global copper mining rates, market supply, copper price and the end of copper reserves. Resour. Conserv. Recycl. 87, 158–174. https://doi.org/10.1016/J.RESCONREC.2014.03.007
- Tizaoui, C., Bouselmi, L., Mansouri, L., Ghrabi, A., 2007. Landfill leachate treatment with ozone and ozone/hydrogen peroxide systems. J. Hazard. Mater. 140, 316–324. https://doi.org/10.1016/J.JHAZMAT.2006.09.023
- US Department of the Interior, 2022. 2022 Final List of Critical Minerals, Federal Register. Office of the Federal Register.
- US DoE, 2011. Critical Materials Strategy. Washington DC.
- US DOE, 2020. Critical Minerals and Materials: U.S. Department of Energy's Strategy to Support Domestic Critical Mineral and Material Supply Chains (FY 2021-FY 2031). Washington DC. https://doi.org/10.3133/70194932
- USGS, 2022a. Mineral Commodity Summaries 2022, Mineral Commodity Summaries. Reston. https://doi.org/10.3133/MCS2022
- USGS, 2022b. USGS.gov | Science for a changing world [WWW Document]. U.S. Dep. Inter. URL https://www.usgs.gov/ (accessed 3.3.22).
- Vahidi, E., Navarro, J., Zhao, F., 2016. An initial life cycle assessment of rare earth oxides production from ion-adsorption clays. Resour. Conserv. Recycl. 113, 1–11. https://doi.org/10.1016/j.resconrec.2016.05.006
- Vahidi, E., Zhao, F., 2018. Assessing the environmental footprint of the production of rare earth metals and alloys via molten salt electrolysis. Resour. Conserv. Recycl. 139, 178–187. https://doi.org/10.1016/J.RESCONREC.2018.08.010
- Vahidi, E., Zhao, F., 2017. Environmental life cycle assessment on the separation of rare earth oxides through solvent extraction. J. Environ. Manage. 203, 255–263. https://doi.org/10.1016/J.JENVMAN.2017.07.076
- Van der Voet, E., Van Oers, L., Verboon, M., Kuipers, K., 2019. Environmental Implications of Future Demand Scenarios for Metals: Methodology and Application to the Case of Seven Major Metals. J. Ind. Ecol. 23, 141–155. https://doi.org/10.1111/JIEC.12722

- Wang, H.T., Liu, Y., Gong, X.Z., Wang, Z.H., Gao, F., Nie, Z.R., 2015. Life Cycle Assessment of Metallic Copper Produced by the Pyrometallurgical Technology of China. Mater. Sci. Forum 814, 559–563. https://doi.org/10.4028/WWW.SCIENTIFIC.NET/MSF.814.559
- Wang, M., Elgowainy, A., Lee, U., Baek, K.H., Bafana, A., Benavides, P.T., Burnham, A., Cai, H., Cappello, V., Chen, P., Gan, Y., Gracida-Alvarez, U.R., Hawkins, T.R., Iyer, R.K., Kelly, J.C., Kim, T., Kumar, S., Kwon, H., Lee, K., Liu, X., Lu, Z., Masum, F.H., Ng, C., Ou, L., Reddi, K., Siddique, N., Sun, P., Vyawahare, P., Xu, H., Zaimes, G.G., 2022.
 Summary of Expansions and Updates in GREET® 2022 (No. ANL/ESIA-22/1). Argonne, IL (United States). https://doi.org/10.2172/1891644
- Wang, M., Elgowainy, A., Lee, U., Bafana, A., Banerjee, S., Benavides, P.T., Bobba, P.,
 Burnham, A., Cai, H., Gracida-Alvarez, U.R., Hawkins, T.R., Iyer, R.K., Kelly, J.C., Kim,
 T., Kingsbury, K., Kwon, H., Li, Y., Liu, X., Lu, Z., Ou, L., Siddique, N., Sun, P.,
 Vyawahare, P., Winjobi, O., Wu, M., Xu, H., Yoo, E., Zaimes, G.G., Zang, G., 2021.
 Summary of Expansions and Updates in GREET[®] 2021 (No. ANL/ESD-21/16). Lemont.
- Wei, W., Samuelsson, P.B., Tilliander, A., Gyllenram, R., Jönsson, P.G., 2020. Energy Consumption and Greenhouse Gas Emissions of Nickel Products. Energies 2020, Vol. 13, Page 5664 13, 5664. https://doi.org/10.3390/EN13215664
- Weng, Z., Haque, N., Mudd, G.M., Jowitt, S.M., 2016. Assessing the energy requirements and global warming potential of the production of rare earth elements. J. Clean. Prod. 139, 1282–1297. https://doi.org/10.1016/J.JCLEPRO.2016.08.132
- Winjobi, O., Kelly, J.C., Dai, Q., 2022. Life-cycle analysis, by global region, of automotive lithium-ion nickel manganese cobalt batteries of varying nickel content. Sustain. Mater. Technol. 32, e00415. https://doi.org/10.1016/J.SUSMAT.2022.E00415
- Wu, W.Y., 2005. Rare-Earth Metallurgy (in Chinese), 1st ed. Chemical Industry Press, Beijing.
- Xia, Y., Lefler, H.D., Fang, Zhigang Zak, Zhang, Ying, Sun, P., 2020. Energy consumption of the Kroll and HAMR processes for titanium production, in: Fang, Z.Z., Froes, F.H., Zhang, Y. (Eds.), Extractive Metallurgy of Titanium: Conventional and Recent Advances in Extraction and Production of Titanium Metal. Elsevier, pp. 389–410. https://doi.org/10.1016/B978-0-12-817200-1.00017-X
- Yang, X.J., Lin, A., Li, X.-L., Wu, Y., Zhou, W., Chen, Z., 2013. China's ion-adsorption rare earth resources, mining consequences and preservation. Environ. Dev. 8, 131–136. https://doi.org/10.1016/j.envdev.2013.03.006
- Yang, Zhaoyue, Yang, Zhendong, Yang, S., Liu, Ziliang, Liu, Zhenghua, Liu, Y., Drewniak, L., Jiang, C., Li, Q., Li, W., Yin, H., 2022. Life cycle assessment and cost analysis for copper hydrometallurgy industry in China. J. Environ. Manage. 309, 114689. https://doi.org/10.1016/J.JENVMAN.2022.114689
- Zaimes, G.G., Hubler, B.J., Wang, S., Khanna, V., 2015. Environmental life cycle perspective on rare earth oxide production. ACS Sustain. Chem. Eng. 3, 237–244. https://doi.org/10.1021/SC500573B/SUPPL_FILE/SC500573B_SI_001.PDF
- Zhang, L.C., Chen, L.Y., Wang, L., 2020. Surface Modification of Titanium and Titanium Alloys: Technologies, Developments, and Future Interests. Adv. Eng. Mater. 22, 1901258. https://doi.org/10.1002/ADEM.201901258
- Zhang, W., Zhu, Z., Cheng, C.Y., 2011. A literature review of titanium metallurgical processes. Hydrometallurgy 108, 177–188. https://doi.org/10.1016/J.HYDROMET.2011.04.005
- Zhu, Q., Tian, C., Xiao, Z., Liu, Z., 2013. Research Progress and Developing Trend of Soil Nitrogen in Ion-type Rare Earth with In-situ Leaching (in Chinese). Nonferrous Met. Eng. Res. 2, 40–43.

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Energy Systems and Infrastructure Analysis Division

Argonne National Laboratory 9700 South Cass Avenue, Bldg. 362 Lemont, IL 60439-4854

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