

**Material and Energy Flows Associated
with Select Metals in GREET2:
Molybdenum, Platinum, Zinc, Nickel, Silicon**

Energy Systems Division

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1. INTRODUCTION

Life-cycle analysis has been effectively used in many fields to quantify the environmental impacts of products and processes. Argonne National Laboratory's GREET model (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation), was originally developed to evaluate fuel-cycle (or well-to-wheels) energy use and emissions of various transportation technologies (Wang 1999). In 2006, the GREET vehicle-cycle model (GREET 2) was released to examine energy use and emissions of vehicle production and disposal processes (Burnham et al. 2006). GREET 2 contains material and energy flow data for the production of over 50 materials that are in the supply chain of the different vehicle types considered in the GREET 2 model, which include conventional vehicles, electric vehicles, fuel cell vehicles, and other vehicle types. Further, the GREET 2 model contains data regarding the composition of different vehicle types and their components (e.g., lithium-ion batteries in the case of electric vehicles). GREET 2 users can estimate life-cycle energy consumption and air emissions (including greenhouse gas (GHG) emissions) for different vehicles and their components. While GREET 1 has been fully expanded to permit calculation of life-cycle water consumption, GREET 2 is still undergoing this expansion as data become available (Lampert 2014).

In general, we consider that the materials contained within GREET 2 are used in the United States. For materials that are not produced in the United States, GREET developers seek material and energy flow data associated with producing these materials in locations that supply a significant share of the material to the United States. For materials produced both domestically and abroad, typical data sources include the academic literature, industry association reports, environmental permits, corporate sustainability reports, and other publicly available data sources. Reports that are not public may be used to corroborate findings, but generally are not used as data sources. For materials produced abroad, when possible upstream data specific to those locations are applied in calculating the cradle-to-gate energy and emissions intensity of the material. If country-specific energy data are available within GREET, emissions factors and efficiencies for that country's electrical grid and/or stationary and mobile power sources are used (GREET has such data for Chile, for instance). In absence of this energy data, U.S. efficiency factors are applied for mobile and stationary (on site) power sources. For electricity, information regarding the given country's electrical grid mix and transmission and distribution losses can be found and used to create a pseudo-country specific grid; however, upstream data and facility efficiencies will commonly be based on U.S. domestic electricity production. Domestically produced materials use domestic GREET fuel-cycle assumptions and calculations related to fuels, energy, and emissions associated with those fuels depending upon assumptions regarding

their combustion (i.e., efficiencies and characteristics associated with different combustion technologies as described in GREET).

GREET analyses typically use mass allocation or economic allocation techniques, depending upon appropriateness and data availability. Generally, when co-products have highly disparate economic values, then economic allocation is the preferable means of allocating co-products, otherwise mass allocation is used. However, system expansion can be used as a means of avoiding allocation by subtracting a co-product's energy and emissions from a production route of interest if a known process is available for that co-product. Finally, GREET uses a recycled content approach for all materials; therefore, it does not include recycling credits for prospective recycling, rather recycling is accounted for based on its current usage within the final product of interest (typically vehicles in GREET).

Metals play a role in a number of processes and materials related to the fuels and vehicles that are included in the GREET model. In this report, we describe additions to and expansions of data for metals production in GREET 2 for nickel, platinum, molybdenum, zinc, and silicon, with one chapter per each metal considered. In some cases, data and results for these metals are used in GREET 1 and we describe that use in this report. For example, in the case of zinc, we describe zinc mining and beneficiation, which could be used in GREET 2 as part of the process of vehicle production. We also describe, however, how zinc concentrate from a zinc mine is further refined to produce catalyst-quality ZnO. This material is not used in calculations in GREET 2, but is referenced in some processes in GREET 1. We explain both the development of the data and analysis for these metals and where they are used within GREET.

2. MOLYBDENUM METAL

2.1 INFORMATION AND STATISTICS

Molybdenum is the principal metal sulfide in large low-grade porphyry molybdenum deposits and as an associated metal sulfide in low-grade porphyry copper deposits. Even though molybdenum is contained in various minerals, only molybdenite or molybdenum disulfide (MoS_2) is suitable for the industrial production of marketable molybdenum products. The Mo content of viable ore bodies ranges between 0.01 and 0.25%.

Molybdenum (Mo) is a refractory metallic element used principally as an alloying agent in steel, cast iron, and super alloys. To achieve desired metallurgical properties of alloys, molybdenum, primarily in the form of molybdic oxide or ferromolybdenum, is frequently used in combination with or added to chromium, manganese, niobium, nickel, tungsten, or other alloy metals. Molybdenum enhances steel's and cast iron's hardenability, strength, toughness, and wear and corrosion resistance (Polyak 2015). It is much less toxic than some heavy metals (e.g., mercury, thallium, and lead), which makes molybdenum an attractive substitute for more-toxic materials (IMO 2015). During the first World War, the demand for molybdenum increased due to its applications both in armor plating and as a substitute for tungsten in steel alloys (Millholland 1941). Molybdenum additives come in the form of melt stock products and

include technical Mo oxide, ferromolybdenum, and Mo metal pellets. Metal products (e.g., powder, Mo metal and Mo-based alloy mill products, and products fabricated from them) are also produced from MoS₂.

Moreover, molybdenum compounds are used in high-pressure and high-temperature applications, as pigments, and as catalysts. Chemical products (e.g., catalysts, polymer compounding additives, corrosion inhibitors, and high-performance lubricant formulation) also result from the mining and processing of ores containing MoS₂. Molybdenum's application as a catalyst prompted the development of material and energy flows for the production of molybdenum compounds to be added into GREET. The specific molybdenum-containing compound that we treat as a catalyst precursor is ammonium molybdate ((NH₄)₆Mo₇O₂₄). Molybdenum-based catalysts have a number of important applications in the petroleum and plastics industries and have been noted for their promise in bimetallic catalysts for the upgrading of lignin to various aromatic chemicals among other products (Alonso et al. 2012).

According to the U.S. Geological Survey (Polyak 2015), in 2014 the domestic production and use of molybdenum was valued at about \$1.8 billion (based on an average molybdenum oxide price). Iron, steel, and super alloy producers consumed 74% of the molybdenum produced domestically in 2014. Table 1 presents the yearly production, consumption, exports, and imports of molybdenum in the United States. Molybdenum production has increased over the last 5 years. Although there was a decline in molybdenum production from U.S. mines between 2011 and 2013, 2014 production exceeded 2010 production by 10%. Moreover, it can be observed that the United States exports most of the molybdenum it produces and that the average price of molybdenum in 2014 was estimated to be 22% less than in 2010. The main countries from which the United States imports molybdenum ores and concentrates are Canada, 44%; Mexico, 28%; Peru, 22%; and Chile, 5% (Polyak 2015). For more information and statistics about molybdenum production and its products, please refer to Polyak (2014).

Table 2 presents the world's mine production and reserves of molybdenum. China, the United States, and Chile are the three primary molybdenum producers (Polyak 2015). Polyak (2015) states that the resources of molybdenum are adequate to supply the world's needs for the foreseeable future.

Table 1. Domestic production, imports, exports of molybdenum consumption (in metric tons of molybdenum) (Polyak 2015)

Parameter	Annual Production				
	2010	2011	2012	2013	2014a
Production, mine	59,400	63,700	61,500	60,700	65,500
Imports for consumption	19,700	21,100	19,800	20,200	23,600
Exports	49,900	56,700	48,900	53,100	55,300
Consumption					
Reported ^b	19,200	19,100	19,400	18,600	19,000
Apparent ^c	28,200	26,100	33,100	29,500	33,900
Price, average value (\$/kg) ^d	34.83	34.34	28.09	22.85	26.90

^a Estimated.

^b Reported consumption of primary molybdenum products.

^c Apparent consumption of molybdenum concentrates roasted to make molybdenum oxide. Apparent consumption is defined as the amount molybdenum produced plus the amount that is imported minus the amount exported.

^d Time-weighted average price per kilogram of molybdenum contained in technical-grade molybdic oxide.

Table 2. World's mine production and reserves of molybdenum (Polyak 2015)

Country	Mine Production		Reserves
	2013	2014 ^a	
United States	60,700	65,500	2700
Armenia	6700	6700	150
Australia	–	–	200
Canada	7620	9500	260
Chile	38,700	39,000	1800
China	101,000	100,000	4300
Iran	4000	6300	50
Kazakhstan	–	–	130
Kyrgyzstan	NA	NA	100
Mexico	12,100	11,000	130
Mongolia	1900	2000	160
Peru	18,100	18,100	450
Russia ¹	4800	4800	250
Turkey	1500	2800	100
Uzbekistan ¹	530	530	60
World Total (rounded)	258,000	266,000	11,000

^a Estimated.

2.2 MOLYBDENUM METAL EXTRACTION AND PRODUCTION

The process to obtain molybdenum and other chemicals from molybdenum disulfide concentrate (i.e., MoS_2) consists of three main steps (Figure 1). First, the MoS_2 is extracted or mined, either as a primary deposit or as a byproduct or co-product of copper mining. The second step is beneficiation or concentration, which consists of crushing, grinding, flotation, and leaching. Additional processing such as roasting and refining also takes place (Figure 1). In this section, some important aspects of this three-step process are discussed (IMO 2015).

According to the U.S. Geological Survey (Polyak 2015), in 2014 molybdenum was produced at 13 U.S. mines. Three of these mines produce molybdenum ore as a primary product: the Climax Mine operates in two Colorado locations, Lake County and Summit County, and the Thompson Creek Mine operates in Custer County, Idaho. About 50% of the global supply of molybdenum is produced as a co-product or as a byproduct of copper mining. In co-product mining, commercial viability is dependent upon the extraction of both molybdenum disulfide and copper-bearing minerals, whereas in byproduct mining molybdenum disulfide is obtained during copper recovery (see Section 2.2.2 for more details on co-production of molybdenum) (Fthanakis et al. 2007). Ten copper mines in the United States also produce MoS_2 : six in Arizona, and one each in Montana, Nevada, New Mexico, and Utah.

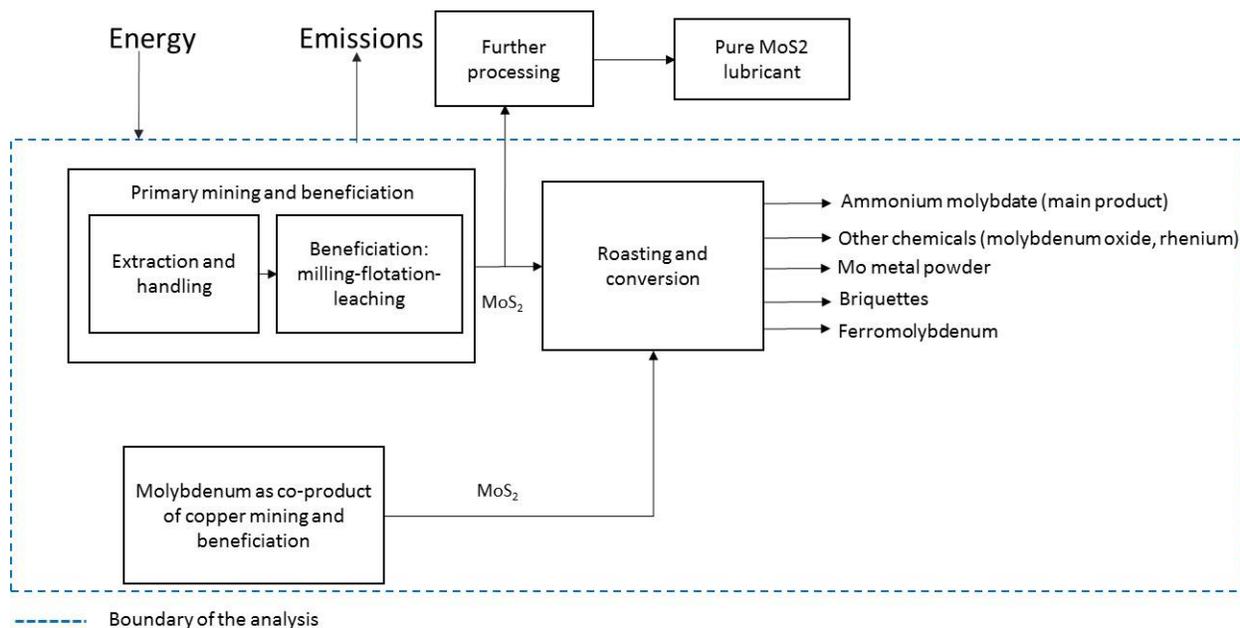


Figure 1. Molybdenum processing flowchart

2.2.1 Primary MoS_2 Mining and Beneficiation

When MoS_2 is the primary mining product, the mining process involves several operations. The first stage is extraction, which includes activities such as blasting and drilling to

loosen and remove material from the mine. There are two conventional hard rock mineral extraction methods: underground and open pit (i.e., surface) mining. Open cast pit technology can be used if the ore lies close to the surface. With this method, the overburden (i.e., rock or soil overlying a mineral deposit) is excavated to reveal the ore body for easy extraction. However, if the ore lies deep underground, the underground block caving technique is employed. In this case, large blocks of ore are undercut and allowed to collapse under their own weight. The resulting rock is removed to the surface for processing (IMOA 2015). Mining also consumes a large amount of explosives, which are used to break up the rock and help in the collection of ore. In fact, most of the explosives and blasting agents sold in the United States are used in mining (Office of Energy Efficiency and Renewable Energy 2002). Two types of explosives can be used in mining: high explosives, which vary in composition and performance, and blasting agents and oxidizers, which include ammonium nitrate-fuel oil (ANFO) mixtures. ANFO is the predominant explosive used in the mining industry because it is not difficult to prepare on the work site and the raw material is inexpensive. In surface mining, for example, the first step is to drill the holes through the overburden, then the explosives are loaded and discharged so the rock in the overburden is shattered. The second stage of mining process is materials handling, which involves the transportation of ore and waste away from the mine to the mill or disposal area.

Once the ore is excavated from the mine, the molybdenum disulfide is concentrated (i.e., in the beneficiation process). The concentration steps are milling, flotation, and leaching. In milling, rod mills crush and grind the mined ore to reduce the rock to fine particles (3–10 mm) in diameter, releasing molybdenum from the rock that surrounds it, called gangue. Flotation, the next step, separates the metallic minerals from the gangue. In this step, the milled ore/gangue powder is mixed with a liquid and aerated so the less dense ore rises in the froth to be collected, while the gangue can be discarded. When copper and molybdenum ores are mined together, the flotation step separates molybdenum disulfide from copper sulfide. The resulting MoS_2 concentrate contains between 85 and 96% MoS_2 (approximately 58wt% of Mo) (Thompson Creek Mining Company 2013). The final step is leaching, which uses acids to dissolve and remove impurities like copper and lead, if necessary.

To estimate the material and energy flows associated with molybdenum mining when there are no co-produced metals, we relied upon a technical report from Thompson Creek Mining Company that describes mining and processing (Marek and Lechner 2011) and the Title V air permits for that facility the Idaho Department of Environmental Quality issued (Thompson Creek Mining Company 2013). Thompson Creek is a molybdenum disulfide concentrate (MoS_2) open pit mining, milling, and concentration facility. The mine annually produces between 15 and 20 million pounds of molybdenum concentrate. Based on the permit, we used a production rate of 20 million pounds MoS_2 concentrate per year (1.14 ton/hr). The plant operates 24 hours per day, 365 days of the year. Moreover, Thompson Creek consumes 10,000 tons of explosives per year, or 1 ton of explosives per ton of molybdenum disulfate (MoS_2) produced. Ditsle (2010) assessed energy consumption and greenhouse gas (GHG) emissions associated with explosives consumed in surface coal mining. He assumed that all operations studied in his report use ANFO as the explosive of mining operations. ANFO's energy content is 2.9 mmBtu/ton (3360 kJ/kg) of explosive. This energy content is somewhat indicative of the energy consumed to produce ANFO, although the actual energy consumed in its production is likely higher than the energy content of the explosives. Using this energy content

and the amount of explosives needed in the Thompson Creek mining process, we estimate that 2.9 mmBtu is consumed per ton of MoS₂ concentrate. This energy is roughly 1% of the total energy inputs used in primary mining and beneficiation. We therefore do not include this energy input in the GREET model. Finally, Thompson Creek also produces lubricant-grade MoS₂ by further processing the concentrate to achieve a higher purity (i.e., 98% or more MoS₂). We do not include the additional processing of MoS₂ to lubricant grade.

Table 3 summarizes the purchased energy inputs required for primary mining and beneficiation processes, which sums to 260 mmBtu/ton MoS₂. Purchased energy refers to the energy delivered to a company and consumed in processes. As shown in this table, to obtain 1 ton of MoS₂ concentrate requires 260 mmBtu, of which 93% is diesel fuel that mining equipment—including hauling trucks, dozers, wheeled loaders and dozers, motor graders, drills, and shovels—consumes (Thompson Creek Mining Company 2013) (see Tables A1 and A2 in Appendix A). As expected, molybdenum mining and beneficiation require high energy inputs because the ore concentration is low. According to Thompson Creek Mining Company (2013) the ore has an assay result of 0.03% of MoS₂ or higher. We also found that hauling trucks consume 54% of the energy consumed by mobile equipment used in the mining process. Stationary equipment including boilers, waste oil heaters, generators, and pumps also consume diesel fuel. Seven percent of the energy consumed is electricity.

Table 3. Purchased energy inputs in primary mining & beneficiation of molybdenum

Fuel Type	mmBtu/hr	mmBtu/ton of MoS ₂ Produced	Fuel Share
Stationary Equipment			
Diesel	62	54	21%
Mobile Equipment			
Diesel	215	188	72%
Electricity	20	18	7%
Total	297	260	—

GREET calculates full fuel-cycle energy consumption and emissions from the combustion of energy inputs such as those reported in Tables 3 and 4. Non-combustion emissions such as particulate matter emissions from materials handling equipment or volatile organic compound (VOC) emissions from chemical reactions or drying equipment must be entered into GREET as separate inputs. In the case of MoS₂ mining, we used data from the Thompson Creek mining permit to estimate non-combustion emissions. Permit emissions data are not-to-exceed limits agreed upon by a facility and a regulatory agency. These data often overestimate actual emissions at a facility. Accordingly, they serve as worst case emissions estimates. Table 4 shows non-combustion total emissions of the process equipment at the mine,

which includes crushers, conveyors, and dryers. The crushing and materials handling equipment have emissions limits for particulate matter between 0.02 and 4 ton/yr of PM_{2.5} and between 0.1 and 14 ton/yr of PM₁₀. In the last part of the concentration process, a filtration step increases the solid concentration of the MoS₂ from 30–35% to 50–60%. A filter is used to remove water. The filter cake is dried in a Holo Flite Dryer that emits at most 16 tons VOC/yr.

The only material that the permit reports to be consumed in the mining operations is hydrochloric acid (HCl), which the leach plant consumes at a rate of 0.013 ton/yr.

Table 4. Non-combustion emissions in MoS₂ mining

Type of Emissions	Primary Crusher (ton/yr)	Overland Conveyor Drive 1 (ton/yr)	East Ore Feeder (ton/yr)	West Ore Feeder (ton/yr)	Holo Flite Dryer (ton/yr)	Total Emissions (ton/yr)	Total Emissions (g/ton of MoS ₂)
PM ₁₀	4.1	4.9	14	14	0.1	36.4	3301
PM _{2.5}	1.2	1.4	4.0	4.0	0.02	10.7	972
VOC	0.0	0.0	0.0	0.0	16	16	1458

The mining industry uses water in the extraction of minerals from the ground and often to wash the ore after it has been extracted. Some operations that use water include crushing, screening, washing, and flotation of the mined material. For example, in Thompson Creek, mine water is added in the crushing and grinding area to crush the ore. According to Thompson Creek Mining Company (2013), the water system is a closed system wherein water and entrained reagents are continuously recycled. This mine tries to recycle as much water as possible to minimize alterations of local fresh water. Water is therefore reclaimed from the tailings pond (where the water is stored) and pumped back to the grinding and flotation plant. The water reclamation system was designed to pump a maximum of 7,750 gallons per minute; 75% of the water is fresh water that is pumped from the Salmon River, while 25% is reused. There are no off-site discharges of mine-influenced water, and surface water drainage from mine operations is directed into the tailings storage facility (Thompson Creek Metals Company, Inc. 2013). Because there is not enough information to quantify the amount of water used in the mining process of molybdenum, we do not include water consumption in this analysis.

2.2.2 MoS₂ Mining as a Co-Product or By-Product of Other Metals

Molybdenum is a byproduct of copper production at the Bagdad and Sierrita Mines in Arizona, which are operated by Phelps Dodge Corp., and at the Bingham Canyon Mine in Utah, operated by Kennecott Utah Copper Corporation (KUCC). Producing about 25% of the copper mined domestically, KUCC is the second largest copper producer in the United States (Rio Tinto-Kennecott Utah Copper Corporation 2014). It also produces gold, silver, and molybdenum at the Utah mine. There, molybdenum is recovered during copper beneficiation, or concentration. Once the copper ore leaves the concentrator as a fine powder, it is put through a series of

flotations where some liquids are added to the powder. These liquids can include xanthates, alcohols, and pine oil (Fthenakis et al. 2009). By adding these liquids, molybdenum, copper, gold, and silver float to the top of the flotation cells in frothy bubbles where they are skimmed off. This process is repeated several times, so that finally the molybdenum disulfide is separated. The concentrate is further cleaned, resulting in a high-quality molybdenum disulfide concentrate, which is about 50 to 58% molybdenum. Then, the molybdenum disulfide concentrate is shipped to roasting facilities (Fthenakis et al. 2009). Table 5 presents production of copper versus production of molybdenum at the Utah mine (Newman et al. undated; Rio Tinto-Kennecott Utah Copper Corporation 2014). The ratio of molybdenum to copper varies by about 3%, depending on the molybdenum grade. Fthenakis et al. (2007) use this 3% ratio as their allocation factor for their calculations (Fthenakis et al. 2007).

Table 5. Cu and Mo production level at KUCC, USA

Year	Cu Refined (ton)	Mo Refined (ton)	Mo/Cu (%)
2001	312,668	8106	2.6
2002	293,700	6100	2.1
2003	230,600	4600	2.0
2012 ^a	162,700	9400	5.8
2013 ^a	193,600	5700	2.9

^a These values are taken from Rio Tinto-Kennecott Utah Copper Corporation (2014).

Fthenakis et al. (2009) report energy consumed in mining and smelting/refining processes associated with co-production of copper, molybdenum, selenium, and tellurium (Fthenakis et al. 2009). Molybdenum, however, is separated off before the smelting and refining steps. We therefore sought to exclude energy consumed in these steps in our estimate of the energy intensity of producing molybdenum as a copper co-product. Fthenakis et al. (2009) reported that concentration is about 50% of the total energy consumed in mining of these metals (25 to 30 GJ/tonne of refined copper). We therefore adopted the energy intensities they report for mining and half the total energy they report for mining and recovery combined as the energy intensity associated with molybdenum co-production. We assume that the energy consumed in concentration is electricity (Norgate and Rankin 2000). Therefore, Table 6 presents the energy inputs for co-produced mining and beneficiation of molybdenum. In addition, Fthenakis et al. (2009) report 54 g of particulate matter emissions from mining per ton of mined metal. We adopt this figure in GREET. Fthenakis et al. also report SO₂ emissions, but these are largely from copper smelting, so we do not include them in molybdenum production.

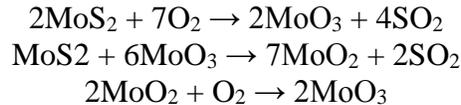
Table 6. Purchased energy inputs for co-produced mining and beneficiation of molybdenum

Fuel Type	mmBtu/ton of Mo ^a Co-Produced	Fuel Share
Mining		
Electricity	1.1	8%
Diesel	1.0	8%
Concentration		
Electricity	11	84%
Total	13	—

^a Mo is molybdenum metal (Fthenakis et al. 2009).

2.2.3 Production of Ammonium Molybdate

The next step in the conversion of MoS₂ to chemical compounds is the roasting of the MoS₂ concentrate to yield molybdenum trioxide (MoO₃) (also known as technical Mo oxide, or tech oxide). Roasters are multi-level hearth furnaces, in which MoO₃ concentrates move from top to bottom against a current of heated air and gases blown from the bottom. Typically, the roaster operates between 500 and 650°C. The chemical reactions that occur in the roaster are as follows (IMO 2015):



The resulting roasted molybdenite concentrate typically contains a minimum of 57% molybdenum, and less than 0.1% sulfur. The MoO₃ is then converted to a number of other products, including ammonium molybdate, which is the product of our interest in this report.

Kumar (2002) and the U.S. Environmental Protection Agency (EPA) (1994) describe the upgrading process and subsequent products in detail. Both EPA (1994) and Kumar (2002) suggest that it is possible to produce several products from MoO₃. Figure 1 presents those products: metal Mo powder, molybdc oxide (MoO), ammonium molybdate (the catalyst precursor), and rhenium. Rhenium is a very scarce metal (1 ppb in the earth’s crust) and its production through MoS₂ concentrate roasting is one of its principal commercial sources.

To estimate the material and energy flows in the conversion of MoS₂ concentrate to products including ammonium molybdate, we used a Title V air permit for Climax Molybdenum Company in Fort Madison, Iowa (Climax Molybdenum Company 2013). Climax Molybdenum Company produces upgraded molybdenum chemical products like lubricant-grade molybdenum disulfide, sublimed pure molybdc oxide, calcined pure molybdc oxide, and different ammonium

molybdate types (i.e., dimolybdate, heptamolybdate, octamolybdate, and sodium). The MoS₂ concentrate comes to this facility directly from different mines and is roasted at temperatures between 500 and 650°C. This concentrate has low moisture content, as dictated by shipping and marketing considerations, usually ranging between 5 and 8% (Thompson Creek Mining Company 2013). The facility uses two roasters. These roasters each have a capacity of 17 tons of MoS₂ concentrate/hr. We assume that these roasters both operate full time and that the MoS₂ concentrate is 90% MoS₂. The permit does not state the output quantities of the different Mo-containing products or of rhenium. To develop material and energy intensity for ammonium molybdate, we used an approach based on conservation of moles of Mo throughout the process. We first calculated energy intensity on a ton-of-pure-MoS₂ basis, then converted those results to a per-ton-of-ammonium-molybdate basis using stoichiometry. The data GREET contains, however, are first presented on a per-ton-of-pure-MoS₂ basis so that a user can trace the data directly to what the permit provides as energy consumption and pollutant emissions data. The mass of rhenium produced is likely very small; we do not assign any material or energy consumption to its production. In addition, 0.18 tons of ammonium hydroxide (NH₄OH) are consumed to produce 1 ton of ammonium molybdate.

The total amount of energy required in the conversion process is presented in Table 7. These values come from dividing the energy consumption of each piece of process equipment by 31 ton/hr (which is the total amount of molybdenum concentrate processed during roasting and conversion). The list of process equipment and their energy consumption values are presented in Table A3 of Appendix A. Then sum of these values is the total energy consumption. 73% of the energy consumed in this process is natural gas while 27% is diesel oil. Although the permit for this section of the process does not include process equipment electricity consumption, this analysis includes the most important, energy-intensive process equipment (such as roasters, furnaces, and kilns).

Table 7. Purchased energy inputs for the conversion of MoS₂ concentrate to ammonium molybdate

Fuel Type	mmBtu/ton of MoS ₂	Fuel Share
Natural Gas	6.5	73%
Diesel	2.5	27%
Total	9.0	–

Table 8 presents non-combustion emissions from conversion of MoS₂ into the products Climax Molybdenum Company produces. These emissions correspond to particulate matter (PM) generated by material handling units and processing units (Climax Molybdenum Company 2013). Similar to energy consumption, the values presented in Table 8 are calculated by dividing the PM value of each unit by the total amount of MoS₂ concentrate processed in the conversion process.

Table 8. Particulate matter emission from non-combustion equipment in the conversion process of MoS₂ concentrate to ammonium molybdate

Unit	PM ₁₀ (g/ton MoS ₂)
MoO ₃ Unload to Storage Bin From Bags and Barrels	313
Pure Oxide Product Screening and packaging	76
Downgrade Calciner Product Bagging (2 units)	32
Downgrade Calciner Combustion (2 units)	9
Dryer	64
Sodium Molybdate Drying, Screening, and Packaging	179
MoS ₂ Transfer from Pit to Storage Bin	184
MoS ₂ Rail Car Unload	184
MoO ₃ Transfer from Roaster to Bin	83
Transfer MoS ₂ from Storage to Roaster	106
Briquetting	60
Lime Dust Unload	177
Lime Transfer to Silo	450
Roasters(2 units)	83
Sublimed Oxide Furnace (2 units)	22
Molysulfide Kiln	6
Molysulfide Kiln Afterburner	6
Molysulfide Kiln Burner	9
AOM Dryer	4
Total	2048

In addition, we also include the SO₂ emissions emitted by the sulfur furnace and the two roasters used in the conversion process; these values are shown in Table 9.

Table 9. SO₂ emissions from furnace and roasters in the conversion process of MoS₂ concentrate to ammonium molybdate

Unit	SO ₂ (g/ton MoS ₂)
Sulfur Furnace Startup Burner	922
Roasters (2 units)	3098
Total	4020

In our analysis of molybdenum, we did not consider secondary production (recycling) of molybdenum because only up to 4% of molybdenum in spent catalyst is recycled (Pomarede 2014).

2.3 ADOPTION OF MOLYBDENUM DATA IN GREET 1 AND GREET 2

GREET 2 contains a molybdenum tab that houses the data summarized in Section 2. This tab reports energy consumption data for primary mining of molybdenum in units of mmBtu/ton MoS₂, assuming 90% of MoS₂ concentrate leaving the mine is MoS₂, with the balance being water and impurities. It reports energy consumption data for Mo mining in concert with copper and other metals as mmBtu/ton Mo.

Full fuel cycle results for each of these processes are reported in Section 2 in the same units. To generate this result, one important assumption is the share of molybdenum that is produced as the primary mine product (Section 2.2.1) or as a co-product with other metals (Section 2.2.2). To allow GREET users flexibility in modeling Mo mining, a user parameter (%_{prim}) can be set to define the share of primary-mined Mo. The default value of this parameter is 50% (Fthenakis et al. 2009).

We use Equation 1 (which uses fossil fuel consumption as a sample result) to calculate the total energy or material use per ton of MoS₂ concentrate:

$$Fossil\ Fuel_{total} = \%_{prim} \times (FF_{prim_min\&Ben}) + \%_{Co-prod} \times \left(FF_{co-pro_min\&Ben} \times 0.58 \frac{ton\ of\ Mo}{ton\ of\ MoS_2} \right) \quad (1)$$

Where $FF_{prim_min\&Ben}$ is the fossil fuel use in mining and beneficiation of primary production, and $FF_{co-pro_min\&Ben}$ is the fossil fuel use in the co-produced mining with copper. The mining and beneficiation of primary production report the energy consumption in terms of mmBtu per 1 ton of MoS₂ concentrate, but the value for co-produced mining is in terms of mmBtu per 1 ton of molybdenum. Therefore, $FF_{co-pro_min\&Ben}$ is multiplied by $0.58 \frac{ton\ of\ Mo}{ton\ of\ MoS_2}$ so that it has the same units as primary production. This value corresponds to the 58% of molybdenum in the MoS₂ concentrate as it is presented by Thompson Creek Mining Company (2013) and Fthenakis et al. (2007).

Finally, the Catalyst tab of GREET 1 reports material and energy consumption for conversion of MoS₂ to ammonium molybdate on a per-ton-of-MoS₂ basis. However, to calculate the results for ammonium molybdate on a per-ton-ammonium-molybdate basis, we multiply the energy inputs in the conversion process by $0.96 \frac{ton\ of\ MoS_2}{ton\ of\ (NH_4)_6Mo_7O_{24}}$. This value is calculated through stoichiometric relations between the amount of MoS₂ concentrate and the amount of ammonium molybdate.

3. PLATINUM GROUP METALS (PGMS)

3.1 INFORMATION AND STATISTICS

The six platinum group metals (PGMs) are platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os). All of them occur together in nature alongside nickel and copper. Along with gold and silver, the PGMs are precious metals and very rare

elements in the earth’s crust. PGMs possess a range of unique chemical and physical properties. They are increasingly used in a variety of environmentally-related and specialty technologies, such as chemical process catalysts (especially in oil refineries) and catalytic converters that treat vehicle exhaust (Mudd 2012). PGMs are found in numerous products, from hard disks to aircraft turbines and industrial catalysts. Around 51% of PGMs are used in catalytic converters while 16% of PGMs are used in jewelry (IPA 2015a). The six PGMs are excellent catalysts and can be employed in pathways to produce biofuels. One interesting characteristic of PGMs in catalytic converters is that they decrease harmful emissions from vehicles (Loferski 2015; Saurat and Bringezu 2008). PGMs can also be used as an alloying agent to improve the wear-resistant properties of electronic components; for example, ruthenium is used to improve this property in titanium, platinum, and palladium (Wang et al. 2013). The GREET catalysis module therefore relies on the material and energy flows for PGM production developed herein.

Besides use in catalytic converters, a key transportation application of platinum is its use as a catalyst in fuel cells. A thin layer of Pt on carbon paper or cloth coats one side of fuel cells’ cathode and anode. At the anode, this coating catalyzes the oxidation half reaction; at the cathode, it catalyzes the reduction half reaction. The Pt catalyst allows fuel cells to operate at low temperatures (Burnham et al. 2006).

Table 10 presents the yearly production, exports, and imports of PGMs in the United States (Loferski 2015). Platinum and palladium are the dominant PGMs in the United States because they are more abundant and higher in value than the other PGMs in Table 10. According to Loferski (2015), in 2014 one domestic mining company produced PGMs at its Stillwater and East Boulder Mines in south-central Montana. Small quantities of PGMs were also recovered as byproducts of copper refining.

Table 10. Domestic production, imports, exports consumption kg of PGMs

PGM	Year				
	2010	2011	2012	2013	2014 ^a
Mine Production (platinum and palladium)^b	15,050	16,100	15,970	16,320	15,850
Imports for Consumption					
Platinum	152,000	129,000	172,000	116,000	130,000
Palladium	70,700	98,900	80,100	83,100	99,000
Rhodium	12,800	13,100	12,800	11,100	11,000
Ruthenium	14,100	13,300	10,200	15,300	11,000
Iridium	3530	2790	1230	1720	2500
Osmium	76	48	130	77	235

Exports (PGMs)^c	61,040	45,820	43,510	39,640	41,700
Price, Average Value (\$/troy ounce)^d					
Platinum	1616	1725	1555	1490	1440
Palladium	531	739	649	730	830
Rhodium	2459	2204	1275	1069	1180
Ruthenium	199	166	112	76	67
Iridium	642	1036	1066	826	573

^a Estimated.

^b Estimated from published sources.

^c Mostly platinum (28%) and palladium (57%)

^d Engelhard Corporation unfabricated metal.

Between 2010 and 2013, the United States imported platinum from Germany (16%), South Africa (16%), the United Kingdom (8%), and Canada (7%), among other countries (53%). Countries from which the U.S. imported palladium include Russia (31%), South Africa (28%), the United Kingdom (23%), Norway (5%), and other countries (13%). The world resources of PGMs are estimated to total more than 100 million kilograms. South Africa has the greatest PGM resource, with the largest PGMs reserves in the Bushveld Complex; 71% of worldwide PGM production occurs in this country. Russia, the site of 14% of worldwide PGMs production, and the United States have the second and third highest PGM reserves, respectively (Loferski 2015). Other PGMs-producing countries include Zimbabwe and Canada, (IPA 2015a).

3.2 PGMs EXTRACTION AND PRODUCTION

PGMs undergo extraction and beneficiation processes that are similar to those described for molybdenum in Section 2.2. Six months can elapse from PGMs-bearing ore recovery to refined metal production because extraction, concentration, and refining of PGMs require complex, costly, and energy-intensive processes. In South Africa, PGMs-bearing ores generally have a low PGMs content (between 2 and 6 g/ton); therefore, to produce 1 ounce (31 g) of platinum requires between 10 and 40 tons of ore (IPA 2015a). Expensive to produce, PGMs are more costly than other metals.

To develop material and energy flows for platinum production in GREET 2, we are adopting data for PGMs production at a South African mine because South Africa produces the majority (71%) of PGMs worldwide. These data serve to update the existing data in GREET 2 for South African PGMs production (Burnham et al. 2006). The mining company operating the mine is called the Anglo American Platinum Company, or Amplats, and it extracts some 40% of the world's newly mined platinum. Amplats operates in the Bushveld Complex, which is the principal source of South Africa's PGMs. This complex includes the Bathopele, Dishaba, Mogalakwena, Siphumelele, Thembelani, and Tumela mines. Table 11 presents Amplats' total production of PGMs, gold, nickel, and copper in 2014 (Anglo American Platinum 2014).

According to this table, 107.50 tons of PGMs and gold were produced in 2014, which accounts for only 0.2% of production by mass. Nickel and copper represented 60% and 40%, respectively, of products from Amplats' mines by mass in 2014 (Anglo American Platinum 2014). Figure 2 presents the steps in the PGM mining and refining process, which are described in the following subsections.

Table 11. Refined production of PGMs, nickel, and copper from Amplats mines in 2014

Product	Tons	% by Mass
Platinum	59.1	0.1
Palladium	38.3	0.1
Rhodium	7.2	0.0
Gold	3.0	0.0
Nickel	31,967	60.3
Copper	20,944	39.5
Total Refined Production	53,018	—

We did not find sufficient information to update the GREET 2 data for PGMs production in the United States.

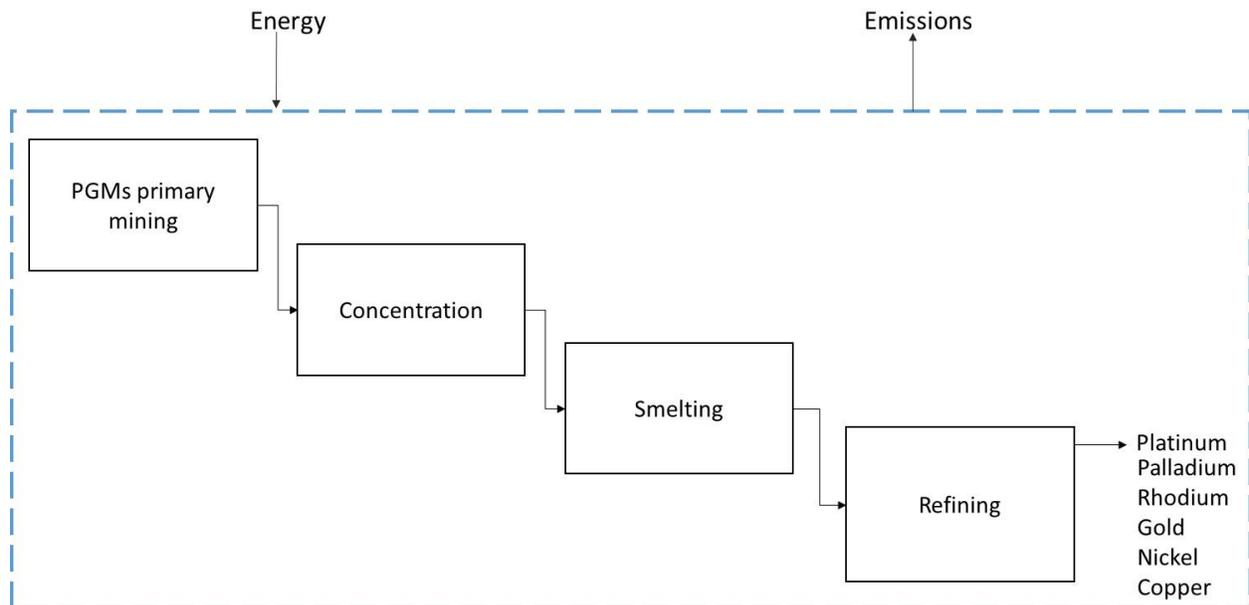


Figure 2. Steps in PGMs, gold, nickel, and copper production. The mining process uses equipment for compressed air, ventilation, refrigeration, and pumps. Concentration includes milling, flotation, and tailing. Smelting equipment includes furnaces and flash dryers. The refining, or purification, section includes boilers and compressors.

3.2.1 Mining

PGMs are mostly mined in South Africa and Russia, but mines in North and South America produce PGMs, nickel, and copper. PGM ores are mined through conventional underground or open cut techniques. The majority of mines in South Africa operate at a depth below 500 m and up to 2 km. Their tabular and narrow ore bodies require intensive mining techniques. PGM ore is drilled and broken with explosives before being removed mechanically to the surface. Factors that contribute to the high energy consumption of mining include ore hauling, the miners' hand-held pneumatic drills consumption of compressed air, and refrigeration of the working areas where the hard rock has a high thermal gradient, or large increases in temperature at increasing depths (IPA 2015a).

3.2.2 Production

On the surface, the ore is crushed and milled into fine particles. Water is added to produce a slurry that is easy to pump. Then, the concentration process separates the milled ore into a waste stream (tailings) and valuable mineral stream by flotation. This separation occurs using a wet chemical treatment that produces a PGMs-rich concentrate that is dried and smelted in an electric furnace at temperatures over 1,500°C. A matte containing the valuable metals is transferred to converters where oxygen-enriched air is blown to oxidize sulfur and iron contained in the furnace matte to SO₂ gas and slag, respectively. The resulting converter matte is slow-cooled to concentrate PGMs into a metallic fraction. The final concentrate is dissolved using hydrochloric acid and chlorine gas. PGMs are then sequentially separated from the base metals nickel, copper, and sometimes cobalt, and refined to a high purity using a combination of solvent extraction, distillation, and ion-exchange techniques (IPA 2015a). Osmium is precipitated as a salt (Anglo American Platinum 2014).

PGMs can also be recovered through recycling (secondary production) (Wilburn and Bleiwas 2004; Johnson Matthey Precious Metals Management 2013). In the United States, secondary production of PGMs uses spent automotive catalytic converters and electronic scrap as a significant resource; however, spent chemicals, reforming catalysts, and equipment used in the manufacture of glass are also another resource of PGMs (Wilburn and Bleiwas 2004). Although the United States is not the primary producer of PGMs, it is the country with the highest platinum and palladium recovery rates. For instance, in 2002 the United States accounted for approximately 65% of the platinum and 70% of the palladium recovered worldwide from catalytic converters; this met 25% of the total U.S. demand for platinum and 20% of its demand for palladium (Wilburn and Bleiwas 2004). Two processes comprise secondary production: (1) the material containing PGMs are either smelted to form a molten metal matte, or dissolved to bring the PGMs into a solution, (2) the PGM-enriched output from step one is then refined to recover the individual metals separately in a pure form identical to that from primary production (IPA 2015b). GREET does not account for the secondary production of platinum because little information is available on energy consumption for this process.

3.3 PGMS PRODUCTION MATERIAL AND ENERGY FLOW DATA

Table 12 presents the purchased energy inputs using two methods to allocate this energy: mass and market value allocation. The first method uses the ratio of each product's weight to the total weight of all products, while the second method involves multiplying the market value of each of the products by the amount produced to generate total monetary revenue for each product (see Table 13). These values are calculated based on the average market value for the last 5 years of each compound produced at Amplats. The revenue shares by product are then used to allocate the total energy use associated with mining and processing operations (Burnham et al. 2006). As is shown in Table 12, the two methods produce dramatically different results. The market-based approach result is two to three orders of magnitude larger than the result obtained by mass allocation. The latter approach is set as the default method in GREET 2. Regardless of the allocation technique, mining and smelting of PGM ores are very resource intensive. The ore typically has a grade of about 5 g/ton of ore (Robb 2005; Renner 1992). Therefore, PGMs primary production generates large amounts of mining waste and consumes large quantities of energy and water. Of the total purchased energy, 35% is consumed during extraction (e.g., mining), while 28% is consumed in smelting processes, and only 12% is consumed during the refining process. Of the total energy, 72.4% comes from electricity, and most of this electricity is used during the concentration process.

Table 12. Purchased energy inputs for the production of a ton of platinum at Anglo American Platinum Company

Process	% of Energy Share	Mass Allocation mmBtu/ton Platinum	Market Allocation mmBtu/ton Platinum
Mining	35	140	73,423
Concentration	24	97	50,759
Smelting	28	114	59,844
Refining	13	53	27,721
Total energy consumption	–	404	211,747

Table 13. Market value for all the products at Anglo American Platinum Company

Product	\$/yr	% by Market Value
Platinum ^a	2,696,416,770	58%
Palladium ^a	776,785,525	17%
Rhodium ^a	341,842,456	7%
Gold ^b	119,859,977	3%
Nickel ^c	545,820,956	12%
Copper ^d	139,711,234	3%
Total	4,620,436,917	–

^a Loferski (2015).

^b George (2014).

^c Kuck (2015).

^d Brininstool (2014).

Table 14 presents fuel share per operation during platinum production (Anglo American Platinum 2014).

Table 14. Fuel Share of Anglo American Platinum Company 2014

Fuel Type	Mining	Concentration	Smelting	Refining	Total Share in the Process
Electricity	70%	99%	70.8%	33%	72%
Diesel/Petrol	30%	1%	0.3%	1%	11%
Coal	0%	0%	25.5%	66%	16%
Natural Gas	0%	0%	3.4%	0.0%	1.0%

On average, electricity production in South Africa is more coal-intensive than in the United States. GREET calculates the energy, GHG, and air emissions intensity of South African–derived PGMs with data for the South African grid mix for 2012 (Table 15). In 2012, most of the electricity produced in South Africa came from coal (93%) and only 5% came from nuclear, which is very different from the U.S. case, where 39% of the electricity comes from coal, 27% from natural gas, and 19% from nuclear power (EIA 2015b).

The South African grid mix data is housed in GREET 1 on the “Input” tab. The user can select this mix using the “User Defined” option. On the GREET 1 “Electric” tab, the electric transmission and distribution loss value is updated to the most current value (from 2011) for South Africa, 8% (World Bank 2015).

Table 15. 2012 South African electricity grid mix

Electricity Source	%
Petroleum	0.1%
Natural gas	0.0%
Coal	92.7%
Biomass	0.1%
Nuclear	5.1%
Hydro	1.9%
Others ^a	0.1%

^a Other refers to electricity which sources come from waste, geothermal, solar, wind.

No data were available on non-combustion emissions from PGM mining, so non-combustion emissions for this process are not included in GREET.

As mentioned before, the mining industry uses significant amounts of water in the extraction and cleaning of minerals. According to Anglo American Platinum (2014), in 2014 the total water consumption was 7.16 billion gallons; 84% of this water was consumed in primary activities, which include mining and processing of platinum group metals, gold, nickel, and copper. The balance was consumed by other activities. Water consumption decreased by 26% in 2014 because of a labor strike. Primary activities consume both new (potable) and make-up water. Potable water is sourced from different water utilities and accounts for 50% of the total water consumption. The fresh water consumed in primary activities is about 113,983 gallons per ton of product (Anglo American Platinum 2014).

4. ZINC

4.1 INFORMATION AND STATISTICS

Zinc oxide has unique physical and chemical properties that make it a multifunctional material. For example, its piezo- and pyroelectric properties allow it to be used as a sensor, converter, energy generator, and photo catalyst in hydrogen production. It can also be used in the ceramic industry due to its hardness, rigidity, and piezoelectric constant, and in the biomedicine industry due to its low toxicity, biocompatibility, and biodegradability (Kołodziejczak-Radzimska and Jesionowski 2014). Zinc oxide comes from processing zinc metal. Although pure zinc metal is never found in nature, it is a natural component of the earth's crust, present in rock, soil, air, and water. The primary source of zinc is sphalerite (or zinc blende or sphalerite [ZnS]), which provides about 90 to 95% of zinc produced today (DOE 2002; International Zinc Association 2015). ZnS occurs in association with other sulphide minerals, especially those of copper, lead, and cadmium. These other sulfides, however, are present in very small proportions

(Wright 1918). For example, analysis of sphalerite in Missouri (Purdue 1912) showed that the composition of the ore is 65.9% zinc (Zn), 33% sulfur (S), 0.25% silicon oxide (SiO), 0.32% iron (Fe), and 0.51% calcium (Ca); in other words, around 98.9% is ZnS, which means that most of the zinc ore is zinc sulfide (Purdue 1912). Zinc ores are widely distributed throughout the world.

Zinc is primarily used as a coating on iron and steel to protect against corrosion. It is also used in vehicle production. Much of the zinc in automobiles is used for galvanization of steel parts, which occurs via hot dipping steel in molten zinc. Zinc makes the average automobile last longer (American Galvanizers Association 2015). However, the amount of galvanized steel in vehicles has been reduced over the years.

According to the U.S. Geological Survey (Tolcin 2015), China is the most significant zinc producer (i.e., 5000 thousand metric tons in 2013). Australia and Peru are also important producers (DOE 2002). In the case of zinc oxide, China, Korea, and Taiwan, are the largest producers, followed by Europe and North America. In North America, where rubber is the major market, consumption of zinc oxide amounted to 207 thousand tons. Around 58% of zinc oxide is used in rubber compounding, 22% is employed in the production of chemicals, 10% is used in agricultural activities, and the rest is used in paints, coatings, ceramics, and other applications (Schlag and Yoneyama 2010).

4.2 ZINC OXIDE PRODUCTION

To produce zinc oxide suitable for catalyst production, the ZnO that comes from roasting zinc concentrate must first be converted to pure Zn through either hydrometallurgical (electrolytic) or pyrometallurgical methods. Figure 3 presents the different steps involved in the production of zinc oxide for catalyst production.

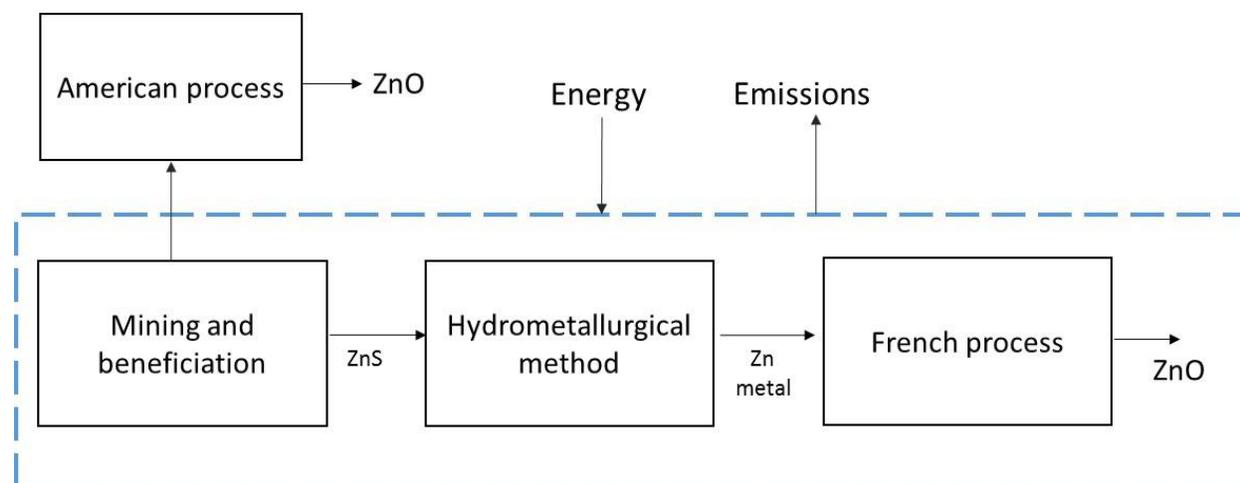


Figure 3. Zinc oxide processing flowchart

4.2.1 Mining and Beneficiation

Eighty percent of zinc mines recover zinc from underground, while 8% have open pits (or surface mining). The remainder recover zinc from a combination of both (International Zinc Association 2015). The use of underground or surface mining techniques depends on the proximity of the ore body to the surface and individual characteristics of the ore body. In underground mining, a tunnel or drift along the vein is created. The ore is removed by drilling and blasting, and removed through the drift to the shaft. The ore is hoisted to the surface for further concentration (DOE 2002). Concentration is needed due to the low zinc content in the ore (which not only contains sphalerite, but also other material that will end up as mining waste). According to the International Zinc Association (2015), zinc ores contain 5–15% zinc. The next process is known as beneficiation; it includes milling, crushing, and flotation steps to produce concentrates of 50 to 60% zinc. Milling is a multistage process that involves crushing followed by wet grinding. The crushed ore is mixed with water and initial flotation reagents to form slurry. Rod and ball mills are used to grind the ore. In flotation, slurry reagents form frothy bubbles that attach themselves to the heavy mineral and allow them to float away from the lighter powdered ore. During or after milling, the ore may be treated with chemicals known as conditioners and regulators to modify the pH of the ore pulp prior to flotation (DOE 2002). The concentrate may contain some copper, lead, and iron. Concentration is usually done at the mine site to keep transport costs to roasters as low as possible (International Zinc Association 2015). Zinc is in the form of ZnS (concentrate) after the beneficiation step.

Table 16 presents zinc mining and beneficiation energy consumption data obtained from different literature sources. After reviewing these data, we choose to maintain the values in GREET from Ruth (1998), 3.7 mmBtu per ton of zinc. We added, however, the energy consumed in the beneficiation process, 0.1 mmBtu electricity per ton of zinc (Norgate and Rankin 2002). Electricity is consumed in the beneficiation process for milling and crushing the rock (Norgate and Rankin 2002). In addition, Norgate and Rankin (2002) also reported that around 228 gallons of water per ton of ore of zinc is consumed in the beneficiation process.

Table 16. Energy inputs required in mining and beneficiation of zinc

Mining	Units	Fuel Type	Beneficiation	Fuel Type	Total	Reference
1.8	mmBtu/ton Zn	None reported	2.9	None reported	4.7	Rankin (2011) ^a
1.7	mmBtu/ton Zn	None reported	2.6	None reported	4.3	
0.1	mmBtu/ton ore Zn	Diesel (62%)	0.1	Electricity (100%)	0.2	Norgate and Rankin (2002)
0.04	mmBtu/ton ore Zn	Electricity (38%)				
2.4	mmBtu/ton Zn	Fuel oil (21%) Gasoline (1%) Electricity (78%)	0.04	Electricity (100%)	2.4	DOE (2002)
0.71	mmBtu/ton ore Zn	Diesel (19%)	None reported		3.72	Currently in GREET 2 (Ruth 1998)
3.01		Electricity (81%)				

^a These values are for Australian conditions.

4.2.1 Metal Production: Hydrometallurgical Method

The most common methods for processing zinc metal are either hydrometallurgical or pyrometallurgical (Porter 1991). Figure 4 describes these two processes (Norgate and Rankin 2002).

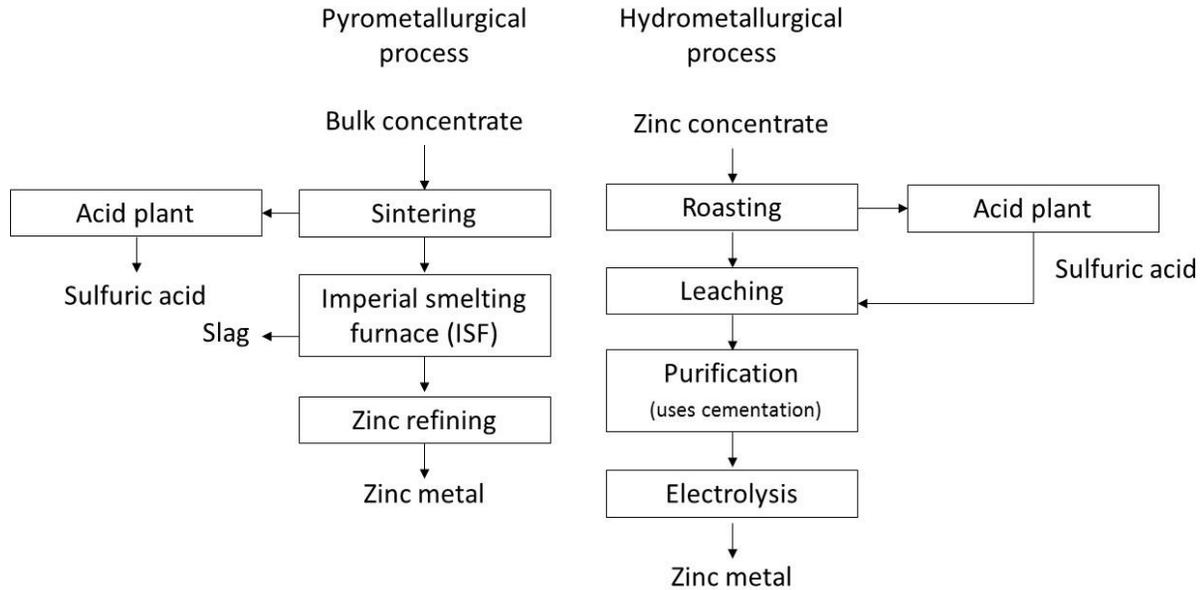


Figure 4. Pyrometallurgical and hydrometallurgical process (based on main processing routes for zinc)

Before metallic zinc can be produced using either hydrometallurgical or pyrometallurgical techniques, sulfur in the concentrate must be removed. This is done by roasting or sintering (International Zinc Association 2015).

The concentrate (ZnS) that is fed to the roasting or sintering steps contains some 25–30% or more of sulfur and different amounts of iron, lead, silver, and other minerals. Roasting is a high-temperature process that converts zinc sulfide (ZnS) concentrate to an impure zinc oxide (ZnO) called calcine (DOE 2002). The concentrate is heated to over $900^{\circ}C$. Simultaneously, sulfur reacts with oxygen, emitting sulfur dioxide that subsequently is converted to sulfuric acid (International Zinc Association 2015). Roaster types include multiple-hearth, suspension, and fluidized beds. Sometimes, zinc ore concentrates are first slurried with water prior to roasting (DOE 2002). On the other hand, sintering is used to compact and form a solid mass of material by heating without melting it to the point of liquefaction. Sintering is essential to prepare the feed for the all thermal methods of producing zinc.

The hydrometallurgical process is also known as the electrolysis process. It includes roasting, leaching, and electrowinning steps. In the leaching stage, sulfuric acid is used to separate zinc oxide from the other calcines. The purification process uses cementation to further purify the zinc. Cementation uses zinc dust and steam to remove other metals like cadmium, copper, cobalt, and nickel from the solution. Finally, in the electrolysis step, to recover the

metallic zinc from the purified solution, current passes through an electrolyte solution which allows zinc to deposit on an aluminum cathode. While the electrolyte slowly circulates through the cells, water in the electrolyte dissociates and releases oxygen at the anode. It is assumed that sulfuric acid is regenerated for recycle to the leach process (EPA 1995). The sulfuric acid acts as a catalyst in the process as a whole. The zinc ingots may have different grades: High Grade (HG) 99.95% and Special High Grade (SHG) 99.99% of zinc (International Zinc Association 2015).

The pyrometallurgical process employs the imperial smelting (IS) process, which reduces zinc and lead into metal with carbon in a specially designed furnace. The IS process is energy-intensive and thus became very expensive following the rise of energy prices. Today, IS furnaces only operate in China, India, Japan, and Poland (International Zinc Association 2015).

According to the International Zinc Association (2015), today over 90% of zinc is produced through the hydrometallurgical process, while 10% of zinc refining is done pyrometallurgically. Norgate and Rankin (2002) put this share lower at 8%. Because the focus of this study is the U.S. zinc industry, we assume that the hydrometallurgical process is used to produce zinc metal.

Table 17 presents the purchased energy inputs to the hydrometallurgical production of zinc metal based on the data reported by Norgate and Rankin (2002) and Moats et al. (2010). The data reported by James et al. (2000) is based on a survey of operating zinc smelters and refineries throughout the world. As presented in Table 17, 37 mmBtu is required to produce 1 ton of zinc metal from Zn concentrate with the hydrometallurgical process. These values also include the energy needed for leaching (8% natural gas) and energy use in the electrolysis step (92% electricity). This latter value includes 11 mmBtu/ton of zinc consumed in the electrolytic cells (Moats et al. 2010), and 3 mmBtu/ton of zinc consumed during roasting and leaching, and in the acid plant (Norgate and Rankin 2002). According to Norgate and Rankin (2002), additional material is required during the hydrometallurgical process: around 3,000 gallons of water per 1 ton of zinc metal produced, 0.090 ton of oxygen per one ton of zinc, and 0.016 ton of lime per ton of zinc metal.

Table 17. Purchased energy and material inputs required in hydrometallurgical production of zinc metal

Stage of Process	mmBtu/ton Zn	Fuel Type	Fuel Share
Leaching	1.1	Natural gas	8%
Electrolysis	13.6	Electricity	92%
Total	14.7		

Material Inputs	Material Intensity
Water (gal/ton Zn)	2948
Oxygen (ton/ton Zn)	0.09
Lime (ton/ton Zn)	0.02

4.2.2 French Process to Produce ZnO

Zinc oxide that can be used as a catalyst is either obtained by a direct process (the American process); or by an indirect process (the French process). According to Kołodziejczak-Radzimska and Jesionowski (2014), in the direct process, the zinc ore is reduced first by heating it with coal such as anthracite, then by oxidizing zinc vapor in the same reactor. All this process occurs in a single production cycle in a furnace which has two layers: (1) zinc ore with coal on top and (2) a coal bed on the bottom. On the other hand, the indirect (French) process occurs in a furnace where the metallic zinc is melted and vaporized at 910°C. ZnO is produced as a result of the zinc vapor reaction with oxygen from the air. According to Brown et al. (1996), the French process burns 0.7 ton of coal per ton of zinc oxide to convert coal and air into reducing gas needed in the vaporizer. The zinc oxide particles exiting a series of furnaces flow through a cooling duct to a bag filter station. The ZnO particles are mainly of spheroidal shape. Zinc oxide from the French process has a higher degree of purity than that produced from the American process (Kołodziejczak-Radzimska and Jesionowski 2014). Because the French process is more prevalent and its product more pure, we assume ZnO catalysts are produced using this technology. Table 18 summarizes the energy input of the French process used in the production of zinc oxide. This information is presented in detail by Brown et al. (1996).

Table 18. Energy consumption in the French process used in the production of zinc oxide

Fuel Type	mmBtu/tons ZnO	% Fuel Type
Electricity	0.1	1%
Fuel oil	22.8	99%
Total	22.9	

Note: 0.7 ton of coal per ton of zinc oxide to convert coal and air into reducing gas (Brown et al. 1996).

Table 19 presents the material balance that indicates the amount of CO₂ emitted as a non-combustion emission. It is important to note that slag is also produced in the French process from burning coal. This slag could emit methane, but we have insufficient data to estimate these emissions. We assumed that all the carbon contained in the coal used in the French process is emitted as CO₂.

Table 19. Non-combustion emissions from coal burning

Type of Coal	%wt Carbon	Total Carbon in Coal (ton C/ton ZnO)	Total CO ₂ Emitted (ton/ton ZnO)	Total CO ₂ Emitted (g/ton ZnO)
Bituminous coal (assumed)	0.61	0.43	1.57	1,425,000

4.3 ADOPTION OF ZINC OXIDE DATA IN GREET 2

GREET 2 contains a zinc tab that presents the data summarized in Section 4. The data on this tab is organized in sections of mining and beneficiation of zinc ore (mmBtu/ton Zn), the hydrometallurgical process (mmBtu/ton Zn), and the French process (mmBtu / ton ZnO).

The energy consumption, air emissions, and water consumption for each of these steps are combined to calculate total impacts of zinc oxide used as a catalyst. To achieve this end, data from mining and the hydrometallurgical processes must be converted to a per-ton-of-ZnO basis with the stoichiometric ratio $0.80 \frac{\text{ton of Zn}}{\text{ton of ZnO}}$.

We use Equation 2 (which uses fossil fuel as an example result) to calculate the total fossil fuel energy consumed per ton of zinc oxide from mine to catalyst as follows:

$$Fossil\ Fuel_{total} = (FF_{min\&Ben} + FF_{Hydro}) \times 0.80 \frac{\text{ton of Zn}}{\text{ton of ZnO}} (FF_{French}) \quad (2)$$

Where $FF_{min\&Ben}$ is the fossil fuel use in mining and beneficiation process, FF_{Hydro} is the fossil fuel use in the hydrometallurgical process, and FF_{French} is the fossil fuel use in the French process. All the calculations are based on the U.S. electricity mix.

5. NICKEL METAL

5.1 INFORMATION AND STATISTICS

Nickel metal is known for its superior malleability, good ductility, high resistance to corrosion, and moderate strength. It is crucial to modern materials; it has important applications in the iron and steel industry for making stainless steel and as an alloy due to its ability to improve strength, toughness, and corrosion resistance. Other major uses of nickel are in electroplating and rechargeable batteries (Kerfoot 2012).

As of 2014, there was only one nickel mine operating in the United States, producing 3.6 metric tons (Mt) of nickel in 2014, which only provided 2.4% of U.S. primary nickel consumption. The majority of nickel consumed in the United States was therefore imported. The imported volume in 2014 consisted of 158 Mt of primary nickel, which is produced from nickel ores, and 39.5 Mt of secondary nickel, which is produced from recycled nickel scraps. During the period of 2010–2013, Canada, Russia, Australia, and Norway were the major import sources for the United States, supplying 36%, 14%, 11%, and 10% of the total imported nickel, respectively. Of the 148 Mt of primary nickel consumed in the United States in 2014, stainless and steel alloy production accounted for 45%, nonferrous alloys and superalloys 43%, electroplating 7%, and the rest went into other usages including batteries, catalysts, and specialty chemicals (USGS 2015).

In this study, we focus on the production of class I nickel, which has a nickel content of 99% or more, and is used for battery and catalyst applications in GREET. Ferronickel, which is the predominant form of nickel consumed in alloy production, is not examined in this study. Furthermore, since the vast majority of recovered nickel is recycled in its alloy state into making stainless steel, steel and other alloys, secondary production is not typical of class I nickel (PE International 2013). We therefore investigate primary class I nickel only.

5.2 NICKEL PRODUCTION

The processes for producing metallic nickel from nickel ore are depicted in Figure 5. There are two types of nickel ores: sulfidic and oxidic (also known as laterites), and the production routes of nickel from the two differ, as shown in Figure 5. Since nickel often coexists with other metals in ores, significant amounts of ferronickel are produced from oxidic ores annually, whereas the production of nickel from sulfidic ores also recovers copper, cobalt, and platinum group metals (PGMs) in descending quantities. In addition, because of the high sulfur content in sulfidic ores, sulfuric acid is also a notable co-product from the pyrometallurgy of sulfidic ores (Kerfoot 2012).

Of the 130,000 Mt of identified nickel resources, 60% is contained in oxidic ores, while the remaining 40% is in sulfidic ones (USGS 2015). Oxidic ores are typically exploited in tropical regions, including the Philippines, Indonesia, New Caledonia, Brazil, and Colombia, whereas sulfidic ores are mostly mined in Russia, Canada, and Australia (USGS 2012). Historically, sulfidic ores were the primary source of nickel, because oxidic ores are more expensive and entail more complex processing (Mudd 2010). In recent years, however, nickel production from oxidic ores has overtaken that from the sulfidic, due to increasing global nickel price and demand, more abundant oxidic ore reserves, decreasing sulfidic ore grades, and improvements in leaching technologies (Mudd and Jowitt 2014).

5.2.1 Mining and Ore Processing

The production of nickel starts with the mining of nickel ores. Sulfidic ores can be exploited through both open-pit and underground mining, while oxidic ores are exclusively open-pit mined (PE International 2013).

Among the sulfidic nickel minerals, pentlandite is the only one of economic significance, which has a nickel content of 0.4–2.0%. This metal content is too low for direct smelting or hydrometallurgy of the ore. The mined nickel ores therefore undergo a beneficiation process, during which the ore is crushed, screened, and then subjected to flotation or magnetic separation, to obtain a concentrate containing 5–15% nickel and copper for subsequent primary extraction. It is worth mentioning that the most abundant nickel mineral is actually nickeliferous pyrrhotite, with a nickel content of 0.5–1.0%. However, because the contained nickel cannot be separated by physical methods, and the pyrometallurgy of pyrrhotites gives off high SO₂ emissions, it is common for nickel producers to reject pyrrhotites to the tailings to reduce energy consumption and undesirable emissions (Kerfoot 2012).

Nickeliferous limonite and garnierite are the two major oxidic nickel minerals extracted (Kerfoot 2012). Oxidic ores typically have a moisture content of ~30%, which is reduced through an ore preparation process involving drying or calcining (PE International 2013). Oxidic nickel ores generally contain 0.8–3.0% nickel. Although the ore preparation process eliminates most of the moisture, the improvement to ore grade through this process is minimal, because the initial nickel concentration is low (0.8–3.0% to 1.1–4.3%) (Kerfoot 2012).

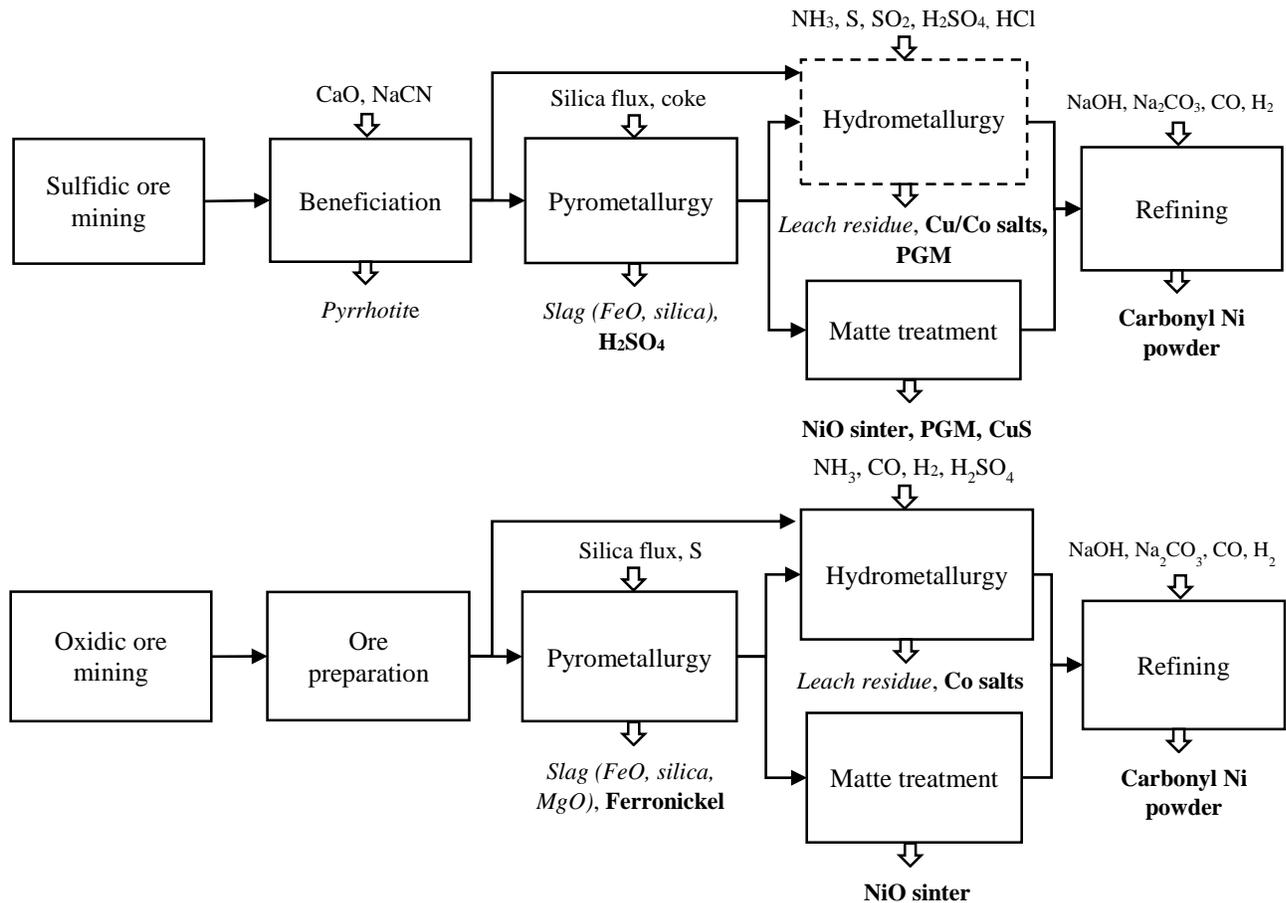


Figure 5. Process flow diagram for nickel production. The dashed box denotes the process not examined in this analysis. Outputs in bold represent co-products, while outputs in italics represent wastes.

5.2.2 Primary Extraction

Prepared oxidic ores and nickel concentrate from the beneficiation of sulfidic ores can undergo either pyrometallurgical treatment to be converted into nickel matte or hydrometallurgical treatment to be converted into a nickel-containing solution. For the nickel concentrate, the pyrometallurgy starts with roasting, during which the concentrate is heated to a temperature of 600–700°C to drive off sulfur as sulfur dioxide and turn the contained iron sulfide into iron oxide. The roasting process generates a significant amount of sulfur dioxide, which is often collected from the off-gas to produce sulfuric acid. The mixture coming out of the roasting process is then sent to a smelter. In the smelter, silica flux is added to the mixture and aids slag formation from iron oxide, gangue and silica. The slag floats on the matte phase, and is separated and discarded. The pyrometallurgical treatment thereby produces a matte with a nickel concentration of 30–50%. The smelting process can be carried out in reverberatory, electric, and flash furnaces, depending on the desired smelting conditions. Following the primary smelting,

part of the remaining iron sulfides in the matte is removed in a converter to produce the final smelting matte (Kerfoot 2012).

The smelting matte coming out of the converter, also known as the converter matte, is high grade, typically containing less than 1% iron and 20% sulfur. It requires further processing to recover nickel, copper, cobalt, and PGMs. Subsequent treatment of this converter matte can be pyrometallurgical, hydrometallurgical, or electrometallurgical. Direct electrometallurgy of nickel matte is not common and is not discussed herein. During the pyrometallurgical treatment, the matte is first poured into a mold at 1000°C, and then cooled to 200°C over a period of 4 days. Because nickel and copper segregate into discrete grains when the matte is cooled slowly, this slow cooling process makes it viable to separate nickel and copper through common beneficiation technologies, such as milling, magnetic separation, and flotation. The process for separating nickel sulfide and copper sulfide is site-specific. Generally speaking, the resulting nickel sulfide concentrate is essentially free of precious metals, and is sent to a roasting plant for further processing, whereas copper and PGMs are recovered through different refining processes. The pyrometallurgical treatment is currently practiced in Russia, China, Botswana, South Africa, and one site in Canada (Kerfoot 2012).

Hydrometallurgical treatment involves leaching the concentrate or converter matte with ammonia or an acid to dissolve nickel and cobalt, while copper is precipitated out as leach residues. Depending on the conditions under which the leaching occurs, hydrometallurgical treatment can be categorized into ammonia pressure leaching, atmospheric acid leaching, acid pressure leaching, and chloride leaching processes. The common output of a leaching process is a nickel sulfate or chloride solution that is copper free, as well as a leach residue that is enriched in copper (Kerfoot 2012). The hydrometallurgical treatment is deployed at nickel sulphide refineries in Australia, Canada, Finland, Norway, Japan, and China (Mudd 2010).

As for prepared oxidic ores, major primary extraction processes include rotary kiln electric furnace, the Caron process, and high-pressure acid leaching (Mudd 2010). During the pyrometallurgical process, the prepared ore needs to be sulfidized before smelting (Kerfoot 2012). Smelting of oxidic ores predominately takes place in rotary kiln electric furnaces (Mudd 2010), where the calcined ore reacts with a reductant to form ferronickel. It should be noted that the smelting of oxidic ores is more energy intensive compared with that of their sulfidic counterparts, because the oxidization of iron sulfide is exothermic, which greatly offsets the energy requirements of the roaster (Kerfoot 2012). Both the Caron process and pressure acid leaching are hydrometallurgical technologies, which selectively extract nickel and cobalt at elevated temperatures using ammonia and sulfuric acid, respectively (Mudd 2010).

5.2.3 Nickel Refining

The final stage of producing high-purity nickel, designated as class I nickel, is refining, during which nickel is generally refined to a purity level >99%. Nickel oxide or nickel matte from the pyrometallurgical treatment can be purified via the electrorefining process or carbonyl process, whereas nickel leach can be recovered by electrowinning or hydrogen reduction.

5.3 CRADLE-TO-GATE LIFE-CYCLE INVENTORIES OF NICKEL

There have been a few LCA studies on nickel production. Mudd collected energy consumption, water consumption, and CO₂ and SO₂ emissions from sustainability reports of leading nickel producers including BHP Billiton, Eramet, Norilsk, Vale, and Xstrata for the period of 1999–2008; compiled the data for each major facility operated by these producers; and calculated the average environmental metrics of these facilities (Mudd 2010). Eckelman obtained energy use and GHG emissions of all major nickel mining, smelting, and refining facilities worldwide during 2005 from publicly available data, and reported the life-cycle energy and GHG intensities for 1 ton of major nickel products, including class I and class II nickel (Eckelman 2010). Norgate and Jahanshahi investigated energy and GHG intensities for various technologies to process nickel laterites, and identified opportunities for impact reduction (Norgate and Jahanshahi 2011). In 2012, the international Nickel Institute (NI) initiated a LCI update for nickel and ferronickel. The study was concluded in 2013 by PE International, resulting in detailed LCI information for each major stage of class I nickel production, representing global industrial averages for the years of 2010–2011. The LCI data were collected from surveyed nickel producers worldwide, which together represent 53% of the class I nickel-producing countries, and 52% of the world production volume (PE International 2013). Another study was conducted by Northey et al. (2014), focusing primarily on the water footprint of the production of copper, gold, and nickel, while material and inventories associated with the production of 1 metric ton of nickel based in Australia for 2011–2012 was also presented (Northey et al. 2014).

Class I nickel-producing companies that participated in the NI study are based in Canada, Australia, Russia, Finland, Norway, Japan, France, and the United Kingdom. Each participating company reported their ore type, processing technology, and production volume. The production volume for 2011 totaled 687,712 metric tons, of which 86% was produced from sulfidic ores by pyrometallurgy exclusively, and the rest from oxidic ores by either hydrometallurgy (12%) or pyrometallurgy (2%). Production information by country, however, was not disclosed in the report (PE International 2013).

As shown in Figure 5, nickel production typically yields various co-products. In the NI study, metal co-products, such as copper, cobalt, iron, gold, silver, and PGMs, were treated by economic value allocation, using the average of the market value over 1997–2011, whereas non-metal coproduct (i.e., sulfuric acid) was treated by system expansion (PE International 2013).

Because the data from the 2013 NI study are more recent and have better geographical coverage, material and energy flows pertaining to class I nickel production reported in the study were chosen to be incorporated into this GREET update, with the exception of water. Water consumption was obtained from the study conducted by Northey et al. (2014), because water usage data is not available from the NI report. Since Northey et al. (2014) reported water consumption for both pyrometallurgical and hydrometallurgical processes, in this analysis the water consumption was calculated assuming a production mix of 88% pyrometallurgy and 12% hydrometallurgy, to be consistent with the 2013 NI study.

The cradle-to-gate LCIs for class I nickel production are summarized in Table 20 (PE International 2013). For comparison, select environmental metrics reported for class I nickel production in the rest of the studies—together with those calculated from the most recent sustainability reports of Norilsk, Vale, and BHP Billiton (Norilsk 2012; Vale 2014; BHP Billiton 2014) based on economic value allocation as employed in the NI study—are listed in Table 21. It should be noted that except for Vale, these companies do not differentiate between their class I and class II nickel products in their reports, and the results are representative of 1 ton of contained nickel.

Table 20. Cradle-to-gate LCI for 1 ton of class I nickel produced

Purchased Energy (mmBtu/ton)	Mining	Beneficiation and Ore Preparation	Primary Extraction	Refining	Total
Resid. oil	–	–	–	–	–
Diesel	4.0	3.0	4.0	4.8	16
Natural gas	8.5	3.9	3.2	29	44
Coal	0.68	1.2	2.9	5.2	10
Electricity	3.8	2.7	5.1	4.7	16

Energy inputs presented in Table 21 exhibit large variation across different regions and processing technologies. Direct comparison of these values, however, is not recommended for two reasons. First, as mentioned earlier, a wide variety of technologies are available for the primary extraction and refining of nickel. These technologies result in substantially different energy consumption. Dramatically different ore grades across regions further drive up the divergence, up to a factor of 20 for 1 ton of contained nickel in the products (Eckelman 2010). Because the facilities investigated by each study may have different combinations of primary extraction and refining technologies, the processes encompassed by the system boundaries are inconsistent and the resultant LCIs vary. Second, as noted in Table 21, the methodologies to treat coproducts adopted by these studies differ. In addition, only some nickel smelters convert SO₂ emissions to sulfuric acid. In the 2013 NI study, the reported co-produced sulfuric acid was modeled by system expansion (i.e., the material and energy requirements pertaining to sulfuric acid production as reported in GaBi 6 database were subtracted from the LCI for nickel production [PE International 2013]). In Eckelman’s (2000) study, the production of sulfuric acid was also credited by system expansion. However, the rest of the studies did not specify whether sulfuric acid was produced at the facilities, and if so, whether any credits were given to it. This led to further divergence of the LCA studies.

In fact, some studies in Table 21 report significantly different energy consumption values for nickel produced in the same region using the identical processing technology. Northey et al. (2014) and Norgate and Jahanshahi (2011) both examined nickel production from 1.3% oxidic ore by high-pressure acid leaching (HPAL) in Australia. HPAL is characterized by large acid consumption, high pressure, and high-temperature autoclaving, and therefore high energy consumption (Norgate and Jahanshahi 2011). However, for the same nickel production pathway, Norgate and Jahanshahi (2011) reported a life-cycle energy consumption of 234 mmBtu/ton,

while Northey et al. (2014) reported a total purchased energy of 590 mmBtu/ton. It can be concluded that the LCA for nickel production is associated with large uncertainty and therefore should receive more attention from worldwide nickel producers and LCA researchers and practitioners.

Table 21. Comparison of life-cycle data for 1 ton of contained nickel

Characteristics	Source							
	Eckelman (2010)	Norgate and Jahanshahi (2011)	Northey et al. (2014)		Norilsk	Vale	BHP Billiton	This Study
Region	World	Australia	Australia		Russia	Brazil and Canada	Australia	World
Ore type	Both	Oxidic	Both		Sulfidic	Both	Both	Both
Product type	Class I	Class I (Ni metal)	Class I (Ni briquettes)		Class I and Class II ^a	Class I	Class I and Class II ^b	Class I
Year	2005	N/A	2011–2012		2011	2014	2014	2010–2011
Process	Both	Hydro (HPAL)	Pyro	Hydro (HPAL)	Pyro	Both	Both	Both
Treatment of coproducts	Mass and system expansion for H ₂ SO ₄	Mass and system expansion for steam	No allocation		Economic	Economic	Economic	Economic and system expansion
Purchased Energy (mmBtu/ton)								
Resid. oil	–	–	–	–	–	–	–	–
Diesel	–	–	6.8	5.5	18	24	17	16
Natural gas	–	–	15	570	210	13	14	44
Coal	–	–	3.0	–	6.6	8.8	7.3	10
Electricity	–	–	23	17	75	16	23	16
Total purchased energy	230	234 ^c	48	590	305	62	61	87
Water consumption (gal/ton)	–	–	16,000	73,000	74,000	38,000	19,000	23,000
On-Site Emissions (g/ton)								
SO _x	–	–	–	–	3,200,000	–	–	1,100,000
PM	–	–	–	–	33,000	20,000	–	13,000
NO _x	–	–	–	–	15,000	–	–	14,000

^a Norilsk is a leading producer of class I nickel.

^b BHP Billiton is a leading producer of ferronickel.

^c Life-cycle energy. Includes sulfur feedstock energy.

It should be pointed out that the LCIs reported herein based on the 2013 NI study do not provide detailed inventories of material inputs for nickel production in the absence of reliable data. The use of explosives for nickel ore mining and the consumption of flocculants in the ore beneficiation process can be sources of substantial GHG emissions (Eckelman 2010). As for the subsequent primary extraction processes, considerable oxygen input to facilitate the oxidization of iron and sulfur in the roasting furnaces is typical for the pyrometallurgy of sulfidic ore, whereas the hydrometallurgy of oxidic ore requires significant amounts of sulfuric acid for leaching (Northey et al. 2014). The use of these materials would incur additional environmental burdens and should be investigated once reliable material-flow data associated with the nickel production becomes available.

Emissions reported in the NI 2013 study and the sustainability reports are on-site emissions, which include emissions from on-site fuel combustion, and process emissions (i.e. non-combustion emissions). Because GREET accounts for combustion emissions already, to avoid double counting the process emissions pertaining to nickel production were estimated by subtracting combustion emissions calculated using GREET emission factors, from the reported on-site emissions in this study. When estimating the process emissions, we focus on PM and SO_x in particular, because they are typical of nickel production (Kerfoot 2012). The reported on-site emissions in NI 2013, calculated combustion emissions, and estimated process emissions are listed in Table 22.

Table 22. Nickel production process emissions (grams/ton)

Emission Type	Mining			Beneficiation and Ore Preparation			Primary Extraction			Refining		
	Report	Comb.	Proc.	Report	Comb.	Proc.	Report	Comb.	Proc.	Report	Comb.	Proc.
PM ₁₀	480	77	400	1,200	240	950	4,900	370	4,600	6,000	610	5,300
PM _{2.5}	240	63	170	590	220	380	2,500	320	2,200	3,000	520	2,500
SO _x	1,400	590	780	1,300	800	480	52,000	1,800	50,000	1,000,000	3,400	1,000,000

Note: Combustion emissions and process emissions do not add up to reported emissions due to rounding.

As shown in Table 20, the production of nickel is electricity intensive. Because the environmental impacts associated with electricity consumption are, by and large, determined by the net consumption amount and the electricity mix, it is imperative to derive an electricity mix that best reflects that of the electricity actually consumed during nickel production. For nickel, the mining and refining processes do not necessarily take place in the same country, so it is also important to assign different electricity mixes to mining and metal production. Two production-weighted electricity mixes are therefore computed based on production shares of ore and metallic metal. The ore production countries are assumed to be where mining and ore preparation occur, so the electricity mix calculated from mine production shares was applied to these two processes. The metallic nickel production countries are assumed to be where primary extraction and refining occur, so the electricity mix calculated from nickel production shares was applied to

them. Because the production shares by country were not reported in the 2013 NI study, the shares were calculated from global production statistics of nickel ore and class I nickel obtained from the USGS (USGS 2012). The 2012 national grid mix and transmission and distribution (T&D) loss data for countries involved in nickel production were obtained from the International Energy Agency (IEA) website (IEA 2015). The two electricity mixes are shown in Table 23 and adopted in GREET.

Energy consumption for nickel production currently in GREET and these from this update are summarized in Table 24. The existing nickel LCI in GREET was based on the LCA study conducted by the Nickel Institute in 2000, representing 55% of global nickel production in 1998 (Ecobalance, Inc. 2000). The Nickel Institute warned against direct comparison of the results from the 2000 and 2013 studies, due to changes in production, data inconsistency, and differences in LCA methodology (PE international 2013). Nonetheless, it can be observed that the energy consumption pertaining to mining and beneficiation and ore preparation increased substantially, potentially due to declining ore grade. The differences in the energy inputs for primary extraction and refining may arise from changes in production mix, treatment of coproducts in LCA (mass allocation and no credits to sulfuric acid in 2000 vs. economic value allocation and credits to sulfuric acid in 2013), processes included in production stages (refining includes matte processing and refining in 2000 vs. refining includes matte refining only in 2013), and technology advancement.

Table 23. Electricity mixes for nickel production

Electricity Fuel Source	Russia	Canada	Australia	New Caledonia	Brazil	Japan	Norway	Finland	Mining and Ore Prep. Mix	Primary Extract. and Refining Mix
Coal	15.8%	10.0%	68.8%	13.8%	2.6%	27.6%	0.1%	16.0%	25.9%	21.7%
Oil	2.6%	1.1%	1.6%	72.4%	3.5%	13.4%	0.0%	0.4%	11.7%	2.4%
Gas	49.1%	10.6%	19.9%	0.0%	8.5%	33.7%	1.8%	9.6%	21.0%	25.6%
Nuclear	16.6%	15.0%	0.0%	0.0%	2.9%	12.3%	0.0%	32.7%	7.8%	11.7%
Hydro	15.6%	60.0%	5.7%	13.8%	75.2%	8.3%	96.7%	23.9%	30.8%	35.3%
Biomass	0.0%	1.4%	0.9%	0.0%	6.4%	2.8%	0.2%	15.4%	1.5%	1.8%
Others	0.3%	1.9%	3.1%	0.0%	1.0%	1.9%	1.2%	2.0%	1.4%	1.4%
T&D loss	10%	5%	5%	7%	16%	5%	8%	3%	8.1%	7.3%
Ore prod. share	25%	21%	25%	14%	14%	0%	0%	0%	–	–
Ni Prod. share	35%	20%	17%	0%	3%	6%	13%	7%	–	–

Table 24. Nickel production purchased energy comparison (mmBtu/ton)

Source	Mining	Beneficiation and Ore Preparation	Primary Extraction	Refining	Total Purchased Energy
GREET 2014	2.7	2.0	110	23	137.7
Update	17	11	15	44	87

6. SOLAR- AND SEMICONDUCTOR-GRADE SILICON

6.1 INTRODUCTION

After oxygen, silicon is the second most abundant element in the earth’s crust, comprising around 28% of the crust’s weight. Silicon is a group IV element with an atomic number of 14 and an atomic weight of 28.09 g/mole. Its density is 2.33 kg/liter. Silicon is normally fairly unreactive, but it does react with alkalis and halogens. It forms halides, hydrides, and oxides and a variety of forms of silicates. Polymers of silicon, known as silicones, also form; one example of this is the siloxane polymers with (Si–O)_x backbones. Silicon and its compounds have many uses, including silicates in glass, ceramics, porcelain, clays, cements, and concrete. Silicon is also used in silica gels, silicone rubber, and fumed silica, and as an alloying element in metal alloys. Further, due to its electrical and semiconductor properties, silicon is also used extensively in the metallic state for electronic devices and solar arrays.

Applications of silicon as a metal are primarily twofold. It is employed: (1) as an alloying agent in aluminum and steel alloys, and (2) in the form of thin metal wafers for solid state devices such as integrated circuits and photovoltaic cells. Applications of the latter include key components of computer and electronic products, which are extensively used in cars and trucks. Further, photovoltaic arrays are increasing their penetration into the power sector including utility and roof-top commercial and residential applications. Metallurgical grade silicon (mg-Si) has a purity ranging from 98.5% to 99.5% (Jungbluth et al. 2012), which is adequate for alloying applications. On the other hand, for electronic applications, the purity of mg-Si is not at all adequate and must be upgraded to impurity tolerances no greater than 0.01 ppmw (parts per million by weight) for solar grade (SoG) silicon and 0.0001 ppmw for electronic grade (EG) silicon (Jungbluth et al. 2012).

The extraordinarily high purity levels needed for electronic and solar application of Si clearly add additional processing steps for their production. Following the production of mg-Si, the material is purified in two separate processes depending on application: (1) production of SoG-polysilicon or (2) production of EG-polysilicon. After these steps come the crystallization processes, which produce either multicrystalline (mc) silicon or single crystalline (sc) silicon. Both multicrystalline and single crystalline silicon are used for photovoltaic applications; electronic applications require single crystalline Si. For clarity purposes, we use the following notation “x-y-Si” for the Si products discussed herein, where x denotes silicon purity grade (SoG

or EG) and γ stands for silicon crystallinity (mc or sc). The EG purity Si used in solar applications is denoted SoG+.

Due to the emergence of photovoltaics as a power source of significant magnitude, a number of authors (Jungbluth et al. 2012; Frischknecht et al. 2015; de Wild-Scholten and Alsema 2005; Alsema et al. 2006; de Wild-Scholten et al. 2006) have conducted life cycle assessments of these systems, especially silicon-based solar cells. The work of Alsema and de Wild-Scholten (de Wild-Scholten and Alsema 2005; Alsema et al. 2006; de Wild-Scholten et al. 2006) is most noteworthy, because early on it provided comparatively detailed material and energy flows for silicon solar cell and array production, all done in collaboration with the photovoltaic industry. The work of both Frischknecht et al. (2015) and Jungbluth et al. (2012) provides the most recent detailed descriptions of the production of solar and electronic grades of silicon wafers. Those reports (Jungbluth et al. 2012; Frischknecht et al. 2015) also cover the life cycles of photovoltaic arrays and assemblies. For the interested reader, Takiguchi (2011), Powell et al. (2012), and Fu et al. (2015) provide information on global flow, economic, and cost analysis for crystalline silicon and polysilicon materials.

The questions at hand are (1) what environmental burdens are associated with the production of metallurgical, solar, and electronic grades of silicon, and (2) what are their contributions to the life cycles of two important products, namely vehicles and solar power generators. To answer these questions, four key life-cycle metrics have been computed for the production of metallurgical grade silicon and electronic and solar grades of silicon wafers. The sections that follow quantify these life-cycle metrics for six unit processes associated with the production of mg-Si, EG-Si, and SoG-Si wafers. They are (1) production of mg-Si; (2) production of high-purity SoG-polysilicon; (3) production of high-purity EG-polysilicon; (4) ingot casting of SoG-mc-Si; (5) crystallization and ingot casting for SoG-sc-Si, and EG-sc-Si; and finally (6) wafer cutting of SoG-mc-Si, SoG-sc-Si, and EG-sc-Si. To provide an estimate of changes in the material and energy intensity of silicon wafers production over the past decade, we also compare these intensities based on recent and older data. Finally, another important objective is to provide updated life-cycle production data in GREET 2 (2015) for mg-Si and SoG and EG grades of silicon wafers.

6.2 METHOD

The system boundary of the process chain for the production of silicon wafers in general is shown in Figure 6. It is comprised of the six unit processes mentioned above. Detailed fuel values for each unit process are listed in Table 25 along with the reference from which they were taken. Our life-cycle characterizations of these processes rely heavily on fuel and power data from Jungbluth et al. (2012) and Frischknecht et al. (2015), although some of that data came from earlier work by de Wild-Scholten and Alsema (2005) for the unit process 2: the purification of mg-Si to high purity SoG-Si. Most of the fuel data listed herein for SoG-Si wafers and mg-Si were taken from Frischknecht et al. (2015). Jungbluth et al. (2012) data were used in Table 25 for EG-Si wafers. Note that the different energy requirements to produce a unit output from unit processes 5 and 6, shown in Table 25, are dependent on both silicon grade and crystallinity.

Subsequently, these unit process data were combined to compute four life-cycle metrics given in Table 26. These metrics are used here to represent the environmental performance of the various process chains and sub-chains required to produce silicon wafers. Depending on the process chain being considered, these metrics could either be gate-to-gate values (any process chain not starting from earth, e.g. process 2 or process chain 2,4,6 in Figure 6) or cradle-to-gate values (any process chain starting at earth, e.g. 1, 2, 4, 6 shown in Figure 6). Process chain results based on unit process data given in Table 25 are presented in Table 26.

The life-cycle metrics employed here to characterize the environmental performance of silicon wafer production are two energy and two GHG emission values. They are (1) direct energy (Edrct), which is the sum of all purchased energy expressed in a common unit (MJ); (2) cumulative energy demand (CED), which is Edrct plus upstream energy production burdens; (3) direct GHG emission (d-ghg), which denotes emissions from all direct operations in the silicon wafer process chain; and finally (4) GHGs, including d-ghg emission plus upstream energy production emissions.

The fuel and power flows covered in this study are the energy inputs needed to drive the unit processes covered here. Also included are all of the upstream energies needed to provide these fuels. All upstream energy and emissions and lower heating values for each fuel or power were taken from GREET 1 2014 (Argonne 2014a). With one exception, the energies required to produce ancillary materials (e.g., HCl) that flow into the various unit processes are not included. The exception is graphite, which is used for and consumed as furnace electrodes in unit process 1. The fuels for the production of graphite are included in a footnote to Table 25.

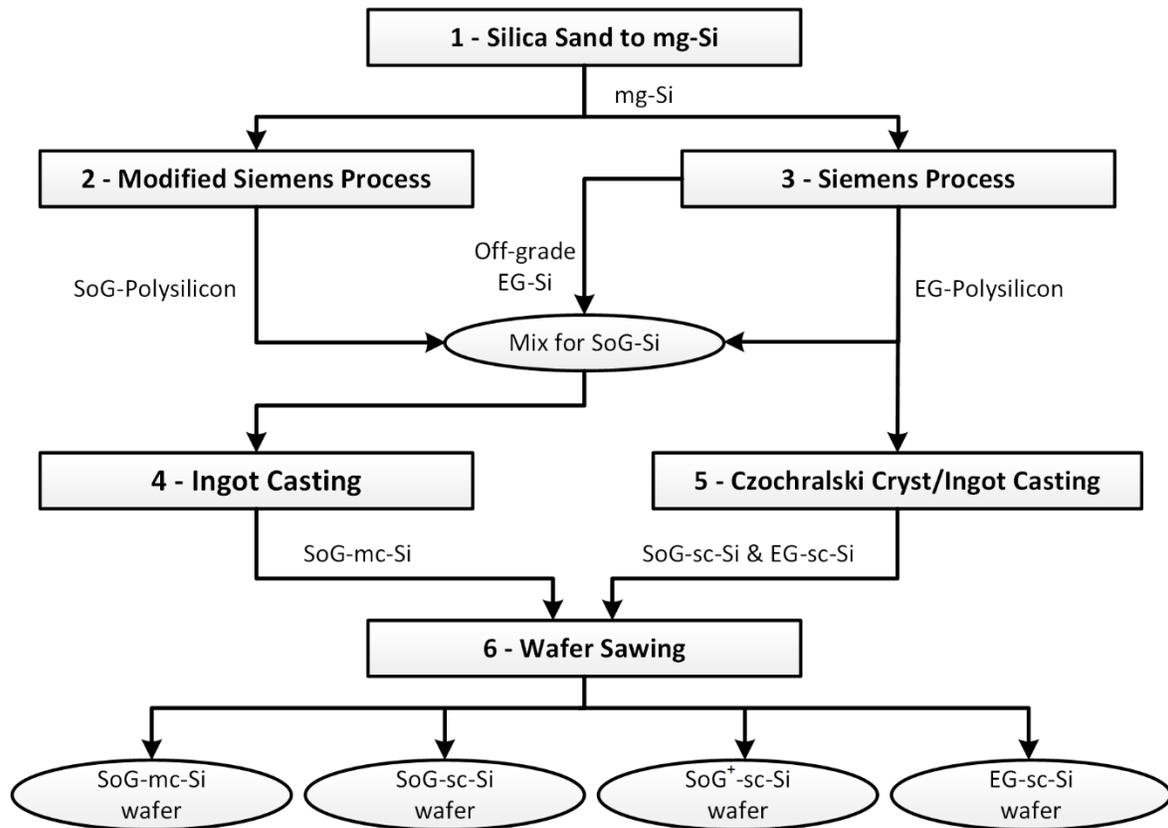
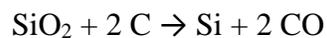


Figure 6. System boundary for the production of photovoltaic and electronic grades of silicon wafers

6.3 UNIT PROCESSES

Figure 6, box 1 clearly shows that the life cycle of the highly refined Si wafers, whether semiconductor or solar grades, start at earth with the production of mg-Si from sand. The feedstocks required to produce mg-Si are silica sand and carbon, which feed the following carbothermic reaction:



The reaction is conducted in an electric furnace, where the outputs of the process are metallic Si, condensed silica fume, and recovered heat. The sources of carbon are a mix of charcoal, wood chips, coal, and coke, the proportions of which vary with the region of production. For example, Si production in Europe (especially Norway) uses mostly coke and coal (Jungbluth et al. 2012) but very little charcoal. On the other hand, woodchips and charcoal are the primary source of carbon for Si production in Australia and Brazil (Jungbluth et al. 2012).

Energy inputs required for producing mg-Si are given in Table 25. Notice that two cited sources of mg-Si data are given there. The data acquired from Boustead and Hancock (1979) represent production processes that were operational during the 1970s and as such are not current. The data for the production of mg-Si extracted from Frischknecht et al. (2015) are more recent, based on data ranging from 1991 to 2002. The processes covered in both references appear to be primarily those in the plant. The mining of silica sand and the transportation of it and carbon feeds to the plant are mentioned in Table 5.1.4.1.1 of Frischknecht et al. (2015); this data yields a transportation fuel estimate of 0.024 liters of diesel per kg of mg-Si, which due to its low magnitude we simply assume fueled ocean, heavy truck, and rail transport. In fact, this diesel consumption turns out to be a very small contribution to the total energy consumed for mg-Si production. A comparison of cradle-to-gate metrics for the two mg-Si datasets (cases 1 and 2) are shown in Table 26. E_{drc} , CED, d-ghg, and GHG values were calculated from the fuels listed in Table 25 using GREET 1_2014. The difference between the two datasets is significant, and can be primarily attributed to the recent Frischknecht et al. (2015) data being more complete than the earlier, more limited, data provided by Boustead and Hancock (1979). For this reason, we henceforth use the Jungbluth et al. (2012) data to represent mg-Si production. To account for the energy and emissions attendant graphite production from petroleum coke the synthetic graphite data from GREET 2_2015 are used.

About 1 million tonnes of metallurgical grade silicon (mg-Si) were produced in the year 2000 (Jungbluth et al. 2012). Because its purity is not adequate for electronic and solar applications, the metal needs to be purified before moving into the casting and cutting processes required to make silicon wafers (see Figure 6).

SoG-Si and EG-Si are derived from much more energy-intensive processes than just producing mg-Si. Fuels required for that process can be found in Table 25. To meet purity levels required for those two materials, considerable energy is required. The Siemens process (Process 3 in Figure 6) is used for the production of EG-Si and the modified Siemens process (Process 2 in Figure 6) is employed for SoG-Si. In both cases the primary route is to grind mg-Si to a powder (grain size <0.5 mm) and dissolve it in HCl, which produces two gases: trichlorosilane (SiHCl_3) and tetrachlorosilane (SiCl_4). These gases are then decomposed on heated Si rods at 1100°C in the presence of H_2 to produce polycrystalline silicon metal and HCl. Metallic impurities do not form chloride gases, thus permitting a gas phase purification of Si. Due to proprietary considerations, process distinctions between the Siemens and modified Siemens processes are not known. This discussion covers both the production of single and polycrystalline silicon; amorphous silicon production is not covered.

Table 25. Gate-to-gate energy and primary material inputs for the production of 1 kg of metallurgical Si, and 1 kg photovoltaic and electronic grades of Si including two types of crystallinity

Parameter	Unit Process										
	1		2		3		4		5		6
Si Grade	mg-Si		Poly-Si prod.		Ingot		Crystlz/ingot		Wafer Sawing		
Crystallinity	mg		SoG		EG		SoG		SoG		EG
Reference	e	f, g	f, g	f, g	mc	f, g	sc	f, g	sc	f, g	sc
Reference	e	f, g	f, g	f, g	f, g	f, g	f, g	f, g	f, g	f, g	f, g
Inputs	Units										
Si flow ^a	kg	–	–	1.13	1.48	1.14	1.07	1.43	2	2	2
Coal	kg	0	0.8	0	0	0	0	0	0	0	0
Pet Coke	kg	0.86 ^b	0.5	0	0	0	0	0	0	0	0
NG	m ³	0	0	5.06	4.77	0	1.86	7.38	0.11	0.11	0.11
Hydrogen	kg	0	0	0	0.090	0	0	0	0	0	0
Diesel	liters	0	0.024	0	0	0	0	0	0	0	0
Wood	kg	0	1.35	0	0	0	0	0	0	0	0
Charcoal	kg	0	0.17	0	0	0	0	0	0	0	0
Graphite	kg	0	0.1	0	0	0	0	0	0	0	0
Electricity	kwh	13.8	11.0	110 ^c	163 ^d	15.5	85.6	200	20.3	25.7	30

^a Material from previous unit process (see Figure 6).

^b Specified as coke but assumed here to be petroleum coke.

^c Specified as 45 and 65 kWh of grid and hydroelectricity, respectively.

^d Specified as 124 and 39 kWh of grid and hydroelectricity, respectively.

^e Boustead and Hancock (1979)

^f Frischknecht et al. (2015)

^g Jungbluth et al. (2012)

A comparison of fuel and power flows for the two processes (unit processes 2 and 3 in Table 25) to produce high-purity SoG-Si and EG-Si reveals a much higher electricity consumption for the latter. E_{direct} , CED, d-ghg, and GHG values for those two processes (cases 3a and 4a) are given in Table 26. The higher electricity consumption in process 3 results in much higher direct and cumulative energy and emissions metrics compared to those for process 2 (see Table 26). The difference is a consequence of the higher purification levels required for EG-Si compared to those for SoG-Si. The output from both of these purification processes is polycrystalline silicon. During unit processes 4 and 5 is when mc-Si and sc-Si are formed (see Figure 6).

When it comes to the production of polycrystalline silicon for photovoltaic applications, all publicly available life-cycle data is for the modified Siemens process. A new process that has been under development employs a fluidized bed reactor (FBR). The FBR approach for producing SoG polycrystalline silicon is described as needing much less energy and hence being more cost effective (Jungbluth et al. 2012; de Wild-Scholten and Alsema 2005; de Wild-Scholten

et al. 2006). Unfortunately, because publicly available life-cycle data for this process are not available, we are unable to include it in our quantitative assessments of SoG-Si wafers.

Also shown in Table 26 are values for E_{drect} , CED, d-ghg, and GHG for cases when extra hydropower beyond normal grid power is used (cases 3b and 4b). Data on the amounts of hydropower used for processes 2 and 3 (see Figure 6) were taken from the cited references (see Tables 1 and 2 for details). As expected, when compared to grid-power-only cases (cases 3a and 4a), there is no impact on direct energy and emissions but there is a significant reduction in CED and GHG. Clearly, hydropower can provide significant reductions in CED and GHG values for Si purification, and hence the subsequent life cycles of SoG-Si and EG-Si products.

Table 26. E_{drect} , CED, d-ghg, and GHG values for the production of one unit (kg or m^2 , as specified) of various Si products via indicated unit process or process chains

Case	Process Chain	Input	Output	% Hydro ^b	Wt ^c kg	E_{drect}	CED	d-ghg	GHG
						MJ/kg	MJ/kg	kg/kg	kg/kg
1	1	Sand ^a	mg-Si	-	1	76	149 ^b	2.7	11.9
2	1	Sand ^a	mg-Si	-	1	110	175	3.6	11.4
3a	2	mg-Si	SoG-Si	0%	1	581	1,161	10.4	84.6
3b	2	mg-Si	SoG-Si	59%	1	581	847	10.4	42.1
4a	3	mg-Si	EG-Si	0%	1	772	1,637	9.8	120
4b	3	mg-Si	EG-Si	24%	1	772	1,449	9.8	94.8
5	1,2	Sand	hp-Si ^f	0%	1	705	1,359	14.5	97.4

WAFERS (1 m^2)									
					kg	MJ/ m^2	MJ/ m^2	kg/ m^2	kg/ m^2
6	1 ^e ,2,4,7	Sand	SoG-mc-Si	0%	0.466 ^d	838	1,654	15	119
7	1 ^e ,2,5,8	Sand	SoG-sc-Si	0%	0.443 ^d	1,260	2,618	18	191
8	1 ^e ,3,6,9	Sand	EG-sc-Si	0%	0.443 ^d	2,106	4,313	33	314
9	See text	Sand	SoG-mc-Si	0%	0.559 ^d	980	1,915	19	138
10	See text	Sand	SoG-sc-Si	0%	0.629 ^d	1,086	2,163	19	156

^a These feeds are silica sand and carbon, the latter generally a mix of charcoal, woodchips, coal, and coke.

^b Percent of additional hydropower (if data available); the balance is U.S. grid power.

^c Mass of output product.

^d Based on wafer thickness (see text).

^e All process chain calculations use Jungbluth et al. (2012) and Frischknecht et al. (2015) data for unit process 1 (see Table 25).

^f “hp-Si” denotes high-purity silicon via modified Siemens process

Polysilicon (high-purity silicon) can be used for more than just photovoltaic and electronic applications; battery anodes are another application. To provide an LCI estimate for

the latter, we generated a cradle-to-gate profile for high-purity silicon, case 5. We assume that processes 1 and 2 are sufficient to provide silicon purity levels for meeting lithium ion battery specifications. E_{direct} , CED, d-ghg, and GHG values for case 5 cannot be directly compared to cases 3 and 4 because case 5 represents a two-process-step process chain, whereas cases 3 and 4 each represent a single process.

After the purification step, the silicon is cast into ingots in processes 4 and 5. In the Czochralski crystallization and ingot casting process, a crystal is slowly extracted from the melt to yield, depending on the feed, either SoG-sc-Si or EG-sc-Si (process 5 in Figure 6). For multi-crystalline Si, a production mix of purified polycrystalline silicon feeds (5.2% off grade EG-Si, 14.6% EG-Si, and 80.2% SoG-Si [Jungbluth et al. 2012]) are melted and cast into ingots of SoG-mc-Si (Process 4 in Figure 6). Fuel and power inputs for processes 4 and 5 are given in Table 25. Notice the significantly greater use of natural gas and electricity for EG-Si versus that for SoG-Si. For the latter, these inputs are solely for melting the production mix, whereas for the single-crystalline silicon fuel and power inputs they are not only for melting purified silicon but also for maintaining temperature during the slow growth of a single crystal. Because there is less processing and greater throughput for SoG-sc-Si, its fuel and power inputs are less than those for EG-sc-Si, which is targeted for electronic circuit applications.

Following processes 4 and 5 is the wafer cutting step, process 6 in Figure 6. Consistent with Jungbluth et al. (2012), it is assumed here that photovoltaic wafers, whether mono- or polycrystalline, are 200 microns thick and electronic wafers are 190 microns thick. Earlier researchers (de Wild-Scholten and Alsema 2005) assumed somewhat thicker wafers, specifically 240 microns for photovoltaic wafers and 270 microns for electronic wafers. Based on the density of silicon, the mass of a square meter of wafer can be computed as follows:

$$Wt = 2330 \text{ kg/m}^3 \times \text{thickness}, \quad (3)$$

where thickness is measured in meters. Fuel and power inputs for sawing cutting of SoG-mc-Si, SoG-sc-Si, and EG-sc-Si wafers are given in Table 25. Notice that the electricity required for cutting photovoltaic wafers is somewhat lower than that for electronic wafers.

Cradle-to-gate (sand to wafer) E_{direct} , CED, d-ghg, and GHG values have also been calculated for SoG-mc-Si, SoG-sc-Si, and EG-sc-Si wafers. See cases 6, 7, and 8 in Table 26 for values. Notice that energy and ghg values are expressed in terms of square meters, which is the appropriate functional unit of silicon wafers. The table clearly shows that of the three cases SoG-mc-Si wafers have the lowest E_{direct} , CED, d-ghg, and GHG values; EG-sc-Si wafers have the highest. In fact, the trend in each metric is as expected (i.e., SoG-mc-Si metrics < SoG-sc-Si metrics < EG-sc-Si metrics). The reason for this is that EG-sc-Si wafers require single crystallinity and ultra-high purity. On the other hand, SoG-mc-Si wafers require lower purity and multi-crystallinity. The four metrics for SoG-sc-Si wafers are intermediate to those of the other two wafers. In some cases, photovoltaic array manufacturers demand higher quality photocells and are willing to pay extra for SoG⁺-sc-Si wafers made from EG-Si. The life-cycle metrics for these wafer materials would be sensibly the same as for EG-sc-Si wafers.

To assess changes in our life-cycle metrics for silicon wafer production between about 2007 and currently, we compare case 6 to case 9 for SoG-mc-Si wafers and case 7 to case 10 for SoG-sc-Si wafers. E_{drc} , CED, d-ghg, and GHG estimates for cases 9 and 10 are also given in Table 26. Results shown in the table for these two cases are based on processes 1 in Table 25 and data taken from a de Wild-Scholten and Alsema (2007) spreadsheet for polycrystalline Si (process 2) and data for their combined processes to make SoG-mc-Si (representing processes 4 and 6) and to make SoG-sc-Si (representing processes 5 and 6). The fuel flow data for their combined processes are: 30 kWh, 0.11 m³, and 0.43, respectively, for electricity, natural gas, and production efficiency for the combined process 4 and 6; and 100 kWh, 2.1 m³, and 0.547, respectively, for electricity, natural gas, and production efficiency for the combined process 5 and 6. Their data (de Wild-Scholten and Alsema 2005) for process 2 is identical to the values given in Table 25.

A comparison of the more recent (Jungbluth et al. 2012; Frischknecht et al. 2015) and 2007 life-cycle metrics in Table 26 are mixed. When normalized by wafer weight, SoG-mc-Si wafers, case 6 has life-cycle metrics close to those of its 2007 counterparts (case 9). For example, the E_{drc} per kg of wafer is 1,798 MJ/kg for case 6 and 1,753 for case 9. These values are nearly the same. On the other hand, for SoG-sc-Si wafers, the normalized recent data (case 6) are greater than those in case 9. For example, E_{drc} for case 7 is 2,844 MJ/kg and for case 10 it is 1,726 MJ/kg. This is primarily due to a lower production efficiency for processes 5 and 6 in case 7 versus case 10. We cannot explain why the production efficiency for the combined process 5 and 6 is less now than it was previously.

6.4 DISCUSSION

E_{drc} , CED, d-ghg, and GHG values for the production of silicon wafers for semiconductor and solar applications are high. This is due to high fuel and power requirements for the production of mc-Si, for its purification to photovoltaic and electronic stock, and for the latter growing single crystal ingots. Note that the production energy for producing mc-Si is already comparable to those for making aluminum and magnesium prior to purification.

The impacts of energy-intensive silicon wafers on their applications are mixed. In the case of automobiles, the amount (in kg) of EG-sc-Si needed for solid state circuits must be small. The authors could not determine the actual amount of EG-sc-Si in solid state circuits on vehicles, but it is likely to be less than 0.1 m² (about a square foot), which amounts to about 0.05 kg of wafer. Based on Table 26, the corresponding CED is 431 MJ, which is small in comparison to vehicle cycle CEDs, typically around 100,000 MJ (Argonne 2014b) or more. The amount of GHGs for this amount of Si is around 31 kg, which is much smaller than around 60,000 kg of fuel-cycle GHGs, depending on vehicle fuel efficiency, over vehicle lifetime.

On the other hand, photovoltaic applications require significant amounts of silicon in the form of thin photoelectric cells needed to capture the comparatively low specific energy of sunlight (watts/m²) to produce electricity. In this case, the production of SoG-Si can have an appreciable impact on life-cycle metrics for solar energy. For example, silicon solar cells generate a peak power of around 145 W/m² of cell surface area, which amounts to 6.89 m² of

cells per kilowatt of solar plant capacity. For 200-micron-thick cells, this amounts to 3.21 kg of SoG-mc-Si per kilowatt of peak capacity. The CED and GHG values for the Si in those cells are 12,328 MJ and 887 kg per kilowatt of peak capacity. These values include production efficiencies of solar cells from wafers (0.943) and arrays from the cells (0.98). The corresponding energy ratio (material E_{in} divided by lifetime electricity out) and emission ratio (GHG per lifetime kilowatt-hour) for just the silicon in the cells are 0.065 MJ/MJ and 17 g GHG/kWh, respectively. For these estimates, we assumed a plant lifetime of 30 years and a plant capacity factor of 20%. This does not include the balance of systems (BOS) for the solar array such as aluminum frame, glass, polymers, and other materials. When BOS burdens are added in, the resulting energy and GHG ratios are about 50% more than those of the Si-only component. Even so, the resulting GHG emission rates (g/kWh), which result only from plant composition and contain nothing from plant operation, are much less than those from fossil power plants that have high plant operational emissions. For example, emission rates for coal-fired power plants are around 1060 g GHG/kWh and around 430 g GHG/kWh for a combined cycle natural gas power plant (Argonne 2014a).

Of the references included herein, the Jungbluth et al. (2012) study provides the only data available for EG-sc-Si wafers. That reference, as well as the Frischknecht et al. (2015) study, provides data for SoG-sc-Si and SoG-mc-Si wafers that are more recent than those by de Wild-Scholten and Alsema (2005, 2007). Due to the more recent vintage, comprehensiveness, and detail of the study, it is concluded that (Jungbluth et al. 2012; Frischknecht et al. 2015) are the most representative of current production of Si wafers for photovoltaic and semiconductor applications and as such are suitable for use in GREET 2 2105.

7. CONCLUSIONS

In this work, we analyzed the material and energy consumption from mining to production of molybdenum, platinum, zinc, and nickel. We also analyzed the production of solar- and semiconductor-grade silicon. We described new additions to and expansions of the data in GREET 2. In some cases, we used operating permits and sustainability reports to estimate the material and energy flows for molybdenum, platinum, and nickel, while for zinc and silicon we relied on information provided in the literature.

Table 27 presents the list of the metals studied here and a comparison between their cradle-to-gate energy and GHG emission intensity values. Solar-grade silicon (assuming a 50/50 market share mix of polycrystalline and monocrystalline silicon) is the most energy intensive and emits the largest amount of GHGs. The primary reason for this energy and GHG intensity is the need for extremely pure silicon, and the requisite heat to obtain that purity. It can be observed that platinum production is the next most energy intensive and emits large amount of GHGs. As presented in this work, mining and smelting of PGMs are resource intensive and require most of the total electricity used in the entire process to produce platinum. One important reason for the high energy intensity of this process is the low PGMs content in ore, which makes the extraction and processing more difficult.

Table 27. Fossil fuel use and GHG emissions of the compounds in the GREET 2

Cradle-to-Gate Result	Molybdenum	Platinum	Zinc	Nickel	Solar-Grade Silicon
Fossil fuel (mmBtu/ton)	583	969	33	102	2,528
GHGs (kg CO2e/ton)	47,640	98,689	3,032	7,947	220,097

One shortcoming of the current work is that we do not account for transporting the finished product to its point of use. One challenge for several of these global commodities is determining the most likely distance of travel for different stages. As noted in the nickel section, the processing may not occur in the same location as the mining, and final delivery entails yet more transportation. It is likely that such transportation will not greatly increase the overall life cycle impacts of the material, but it would benefit this analysis if such steps were examined.

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APPENDIX A

Tables A1 and A2 present fuel consumption rates for fuel burning and mobile combustion equipment used in the mining and beneficiation of MoS₂. These data underpin the purchased energy values in Table 3.

Table A1. Fuel combusted in mobile equipment during mining process

Parameter	Equipment						
	Hauling Trucks	Dozers ^a	Wheeled Loaders ^b	Motor Graders ^c	Wheeled Dozers ^d	Drills ^e	Miscellaneous ^f
Fuel Type	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	Electricity and diesel
Annual Operation (hr/year)	175,200	43,800	26,280	35,040	26,280	35,040	14,760
Fuel Consumption Rate (mmBtu/hr)	127	40	12	3	4	25	25

^a Assuming model Dt6 medium dozers (Caterpillar 2014).

^b Assuming medium conditions load factor (Bise 2013)

^c Assuming average values of motor grades types K and M (Caterpillar 2014).

^d Assuming average values of types 814F (Caterpillar 2014).

^e Assuming Caterpillar engine type C32 (Caterpillar 2009).

^f Miscellaneous equipment refers to shovels (electric and hydraulic shovels). Assuming Caterpillar C18 for hydraulic shovels (Caterpillar 2014) for electric shovels Bucyrus 495HD (Caterpillar 2011) and P&H 2300 XP shovel (JoyGlobal 2015).

The fuel consumption rates from the Thompson Creek reports (in units of hr/year in their permit) must be converted to units of energy per time for inclusion in the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation model (GREET). The Thompson Creek mining technical report provides the type and model of most of the equipment used (Marek and Lechner 2011). We estimated hourly fuel consumption rates for these pieces of equipment based on data from their manufacturers' websites and handbooks. We multiplied the hourly volumetric fuel consumption rate by the lower heating value of diesel (128,450 Btu/gal) to calculate the energy consumption rate. In the case of hauling trucks, we used Equation A1 to compute the fuel consumption (FC) (Keccojevlc and Komljenovic 2010):

$$FC = \frac{CSF \cdot P \cdot LF}{FD}, \quad (A1)$$

where FC is hourly fuel consumption, CSF is the engine-specific fuel consumption at full power (0.24kg/kW/hr), P is power of the engine (1320 kW), LF is engine load factor, and FD is the fuel density (0.85 kg/l for diesel). For the LF, we used 50%, recommended for heavy rock ripping, push loading, and bull dozing in hard rock when working on rock surfaces. The power is based on a Caterpillar 789C hauling truck (RitchieSpecs 2015).

Table A2. Fuel combusted in stationary equipment during beneficiation of MoS₂

Parameter	Equipment							
	Boiler #1	Boiler #2 (hot oil boiler)	Waste Oil Heater (4 units)	Motivator Generator	Mill Auxiliary	Pump Back	Tailing Pump 1	Tailing Pump 2
Fuel Type	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel	Diesel
Consumption Rate (gal/hr)	47	13	4	NR ^a	NR	NR	190	190
Consumption Rate (mmBtu/hr)	6	2	1	10	2	3	18	18

^a NR = not reported.

Table A3 presents the process and material handling units and their capacity involved in the conversion of MoS₂ concentrate to ammonium molybdate at the Climax molybdenum company.

Table A3. Unit operations and material handling equipment for conversion of MoS₂ concentrate

Equipment	Capacity (mmBtu/ton MoS ₂)	Fuel Type
Process Units		
Roaster 1 Burner	0.62	Natural gas
Roaster 2 Burner	0.62	Natural gas
Roaster 1 Burner Heat-up	0.62	Natural gas
Roaster 2 Burner Heat-up	0.62	Natural gas
Boiler #1	0.98	Natural gas
Boiler #2	0.98	Natural gas
Boiler #3	0.73	Natural gas
Molysulfide Kiln Afterburner	0.10	Natural gas

Table A3. (Cont.)

Equipment	Capacity (mmBtu/ton MoS ₂)	Fuel Type
Process Units		
Molysulfide Kiln Burner	0.03	Natural gas
Molysulfide Kiln (inert gas generator)	0.02	Natural gas
Alliant Generator (5 units)	2.42	Diesel
Downgrade Calciner Combustion (2 units)	0.16	Natural gas
ADM/PO Calciner #1	0.13	Natural gas
Sulfur Furnace Startup Burner	0.81	Natural gas
Material Handling		
Fire Pump Diesel Engine	0.06	Diesel
Rail Car Thawing	0.11	Natural gas
Briquetting	0.03	Natural gas
NaMoO ₃ /ADM/AOM Drying, Screening and Packaging	0.01	Natural gas
Furnace start up	0.81	Natural

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