Life cycle assessment of the conventional and solar thermal production of zinc and synthesis gas

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Abstract

The current industrial productions of zinc and synthesis gas are characterized by their high energy consumption and their concomitant environmental pollution. Emissions of greenhouse gases (GHG) could be reduced substantially by combining both productions and by replacing fossil fuels with concentrated solar energy as the source of high-temperature process heat. The extent of such a GHG mitigation has been quantified by conducting a Life Cycle Assessment on the solar- and fossil-fuel-based processes. Total GHG emissions for the conventional zinc production are 3.14 CO_{2-eq} per kg primary zinc (99.995% purity), of which 64% are derived from the electricity consumption in the electrolytic step. Total GHG emissions for the conventional syngas production are 1.04 CO_{2-eq} per kg syngas (molar ratio $H_2/CO=2$), of which 84% are derived from the combustion of fossil fuels in the endothermic steam-reforming step. Total emissions for the solar combined process are 1.51 CO_{2-eq} per 1 kg zinc and 0.527 kg syngas, of which 78% are derived from the pre-/post-processing of reactants and products of the solar reactor, and 16% are derived from their transportation to/from the solar site. However, CO_{2-eq} emissions derived from the solar processing step and its infrastructure are negligible. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Zinc and synthesis gas (syngas) are important commodities. About 50% of the seven million tons of zinc produced each year is used in the galvanizing industry [1,2], while about 50% of the 2.06×10^{12} m³ of syngas produced each year is used for ammonia production [3]. Zinc and syngas are also attractive fuels. Zinc finds applications in zinc/air fuel cells and batteries, and it

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can also be reacted with water to form hydrogen that can be further processed for heat and electricity. Syngas can be used to fuel high-efficiency gas turbines, and it can also be converted to a wide variety of synthetic liquid fuels, including methanol — a promising substitute for gasoline for fuelling cars.

However, the current industrial production of both zinc and syngas carries severe environmental consequences. The current commercial production techniques are characterized by their high energy consumption and their concomitant environmental pollution. Zinc is principally produced by electrolysis and the electric energy input exceeds 10 MJ/kg zinc [4,5]. Syngas is principally produced by catalytic reforming of natural gas, and the thermal energy input exceeds 10 MJ/kg syngas [3]. During these energy-intensive processes, large amounts of greenhouse gases (GHG) and other pollutants are released mostly from the combustion of fossil fuels for heat and electricity generation. These emissions could be reduced substantially and even eliminated completely by using concentrated solar radiation as the energy source of high-temperature process heat [6–8].

In previous papers we have proposed a novel solar thermochemical process, called "SynMet", for the co-production of zinc and syngas gas by combining the reduction of ZnO with the reforming of natural gas [9–11]. The overall reaction is represented by:

$$ZnO + CH_4 \rightarrow Zn + 2H_2 + CO. \tag{1}$$

Natural gas is used exclusively as the reducing agent of ZnO while being reformed to high-quality syngas. High-temperature process heat is supplied by concentrated solar energy. The chemical thermodynamics and kinetics for reaction (1) have been reported in previous studies [9,10]. The reaction is highly endothermic ($\Delta H^\circ_{1250\ K} = 442$ kJ/mol) and proceeds to completion at temperatures above about 1250 K. The technical feasibility of the SynMet process has been demonstrated for a 5 kW solar reactor tested in a high-flux solar furnace [11], and the results suggest that the reactor technology can be developed on an industrial scale. A recent economic assessment for an industrial-scale solar chemical plant indicates that the SynMet process might be competitive with conventional fossil-fuel-based processes at current fossil fuel prices, even before the application of government subsidies and/or credit for pollution avoidance [12].

Separate solar processes for the production of zinc and syngas have also been developed and experimentally demonstrated [13–15]. The advantage of combining both processes would be three-fold: (1) the reforming of natural gas in the absence of catalysts and with proper optimization may be made to produce high-quality syngas with an H_2 to CO molar ratio of 2, which is especially suitable for methanol synthesis; (2) the gases evolved from the ZnO reduction are sufficiently valuable commodities to justify their collection, eliminating inherent gas emissions to the environment; and (3) the integration of ZnO reduction and natural gas reforming into a single reactor could improve energy efficiencies through concurrent high-temperature reactions.

The SynMet process promises a significant reduction of GHG emissions, as compared with the conventional fossil-fuel-based processes for producing zinc and syngas. The extent of the GHG mitigation can be quantified by conducting a Life Cycle Assessment on both the solar- and the fossil-fuel-based processes. The aim of this study is to determine the environmental benefits and drawbacks of an industrial-size application of the SynMet process to co-produce zinc and syngas, weighted against the conventional production of these two commodities.

2. The Life Cycle Assessment

Life Cycle Assessment is a method for evaluating the environmental burdens associated with a product, process or activity by identifying and quantifying energy and materials used and wastes released to the environment. The assessment includes the entire life cycle of the product, process or activity, encompassing extraction and processing of raw materials, manufacturing, transportation and distribution, use/re-use/maintenance, recycling, and final disposal [16,17]. There are various pollution types that may be considered, e.g., GHG emissions, ozone depletion, acidification, human/ecological toxicity. In this study we focus only on the GHG emissions, because the major advantage expected of the SynMet process is a substantial reduction in GHG emissions. For simplicity, only the three most relevant GHG are considered, namely: CO_2, CH_4 and N_2O. The amount of CH_4 and N_2O emitted over the entire process is converted into CO_2 equivalents ($CO_{2\text{-eq}}$) by using the Global Warming Potential factor of 21 for CH_4 and 310 for N_2O.

The Life Cycle Assessment methodology consists basically of three tasks. First, an inventory data of inputs and outputs is established for each process route by determining the material and energy expenses, including transportation and infrastructure. Second, the share of GHG emissions is calculated for each process step and converted into $CO_{2\text{-eq}}$. Finally, $CO_{2\text{-eq}}$ emissions are summed up over the entire life cycle. The total amount of $CO_{2\text{-eq}}$ emissions establishes a basis to compare the environmental impact of producing zinc and syngas via either the SynMet solar process or the conventional fossil-fuel-based processes.

Three processes are in focus: (1) the conventional production of zinc by electrolysis; (2) the conventional production of syngas by steam reforming of natural gas; and (3) the solar co-production of zinc and syngas by the SynMet process. It is of major importance to apply equivalent system boundaries for processes that yield identical products of equal amounts and quality. Therefore, the starting point is set to be the extraction of the raw material; the final product is set to be 1 kg of zinc, in the form of ingots and with a purity of 99.995% (conforming to Deutsche Industrie-Norm #1708 [26]), and 0.527 kg of syngas at 70 atm (pipeline pressure) and of approximate composition 67% H_2 and 33% CO. Such a syngas quality is the one resulting from the SynMet process and is particularly suitable for the synthesis of methanol and other Fischer–Tropsch fuels.

The following section briefly describes the methodology. A detailed description of each process step and its inventory of energy and materials are found in Ref. [18]. Data have been extracted from various sources, the most important are Refs. [1,3–5] for conventional zinc production, Refs. [1,3,21] for conventional syngas production, and Refs. [6–12,23,24,30–32] for solar SynMet production. The background inventory data for the material, energy and transport expenses are taken from Refs. [19,20,22,33].

2.1. Assumed system boundaries

2.1.1. Frame of time

Reference time is set to the year 2020 for which the realization of an industrial-sized 30 MW SynMet solar plant is expected to be technically and economically feasible. This time frame has above all consequences for the composition of the electricity mix. Table 1 shows the 1995 European electricity mix [25] and the predicted mix for the year 2020. The share of renewables, including hydro, is assumed to be 14.8%.

Table 1
European electricity mix (in % share) for the year 1995 [25], and the predicted mix for the year 2020 assumed in this study

Source	Year 1995	Year 2020
Hydro	15.3	12.9
Nuclear	37.1	31.9
Hard coal	17.3	15.5
Lignite	10.3	8.7
Oil	8.6	5.3
Natural gas	8.5	17.0
Other fossil fuels	0.8	3.2
Others (wastes, etc.)	1.7	3.7
Renewables (without hydro)	0.5	1.9

2.1.2. Frame of location

The conventional production plants for zinc and syngas are assumed to be located in Central Europe because mainly European data sources were used in this study. Central Europe is also assumed to be the ultimate delivery/consumer area. As for the solar plant, since it is dependent on the availability of high solar insolation ($>2000\,kWh/m^2/yr$), its location is assumed to be in sunny and desert regions of the earth's sunbelt, e.g., in North Africa. Natural gas reserves are assumed to be in the proximity of the solar plant, but zinc ore deposits are at most 5200 km away. The products of the solar plant need to be transported a maximum of 1500 km to the consumer site. Similar transport considerations but with somewhat different distances apply when the consumer site is located in North America or Japan, and the solar plant is located in Central America or Australia, respectively. For a representative central European case, Table 2 lists the distances assumed and the transportation means for the transportation of raw materials (zinc ore and natural gas) from their extraction site to the production site, and for the transportation of products (zinc and syngas) from the production site to the final delivery/consumer site. Zinc ore and zinc are assumed to be transported by ship and railway, natural gas by pipeline, and syngas

Table 2
Assumed means of transportation and average transport distances of raw materials (zinc ore and natural gas) from their extraction site to the production site, and of products (zinc and syngas) from the production site to the delivery/consumer site

	Transportation to/from							
	Conventional zinc plant		Conventional syngas plant		Solar SynMet plant			
	Zn ore	Zn	Natural gas	Syngas	Zn ore	Zn	Natural gas	Syngas
Railway (km)	500	0	0	0	1000	500	0	0
Ship (km)	3150	0	0	0	4150	1000	0	1000
Pipeline (km)	0	0	200	0	0	0	100	500

by pipeline and ship (but syngas transportation by ship, either in compressed manner or liquefied as methanol, is not yet practised commercially and may incur high costs).

2.1.3. Frame of production size

The reference yearly production rate capacity is 50,000 mt (metric tons) of zinc. This is a European averaged mid-sized plant that would cover about 0.7% of the world zinc supply [1,2]. The corresponding production of syngas is 24,615 mt/yr (or 164×10^6 kWh/yr, assuming a Low Heating Value of 767 kJ/mol).

2.2. Conventional production of zinc — overview

Fig. 1 shows the process chain for conventional zinc production [4,5,26]. Mass balance is normalized for the production of 1 kg primary zinc. The main operation stages are listed as "modules" in the process chain. The starting point is the zinc ore, usually sphalerite, obtained by underground mining. The ore is comminuted by means of crushing and grinding to fine particles which facilitates subsequent separation of unwanted material (gangue) using floatation techniques. The zinc concentrate that results after separation contains typically 45–60% zinc, 30% sulfur, and various minerals of iron, lead, cadmium and copper. It is dried, stored, and finally transported to the primary metal producer site [4]. Both the electrolytic and the carbothermic zinc extraction require ZnO as feed materials, obtained by roasting the zinc concentrate in air at 1300 K. The overall, simplified reaction is represented by:

$$ZnS + 1.5O_2 \rightarrow ZnO + SO_2. \tag{2}$$

Thus, the sulfur content in the concentrate evolves as sulfur dioxide, which is recovered from the off-gases and processed further to sulfuric acid.[1] Any mercury present in the concentrate evaporates and is extracted from the roaster exhaust gas in the form of calomel. The solid product is called calcine and contains approximately 60–63% ZnO, 1–3% sulfur, the remainder being oxidic impurities. Over 80% of the world zinc production is carried out electrolytically. The calcine is treated in a leaching process where it is dissolved in a dilute sulfuric acid solution to form $ZnSO_4$(aq). Insoluble leaching residues, such as zinc ferrites, are precipitated by adding ammonia, and finally sent to tailings ponds for disposal. Typical temperatures for leaching are 333–373 K. Further impurities, such as copper, cobalt and cadmium, are also precipitated from the leachate by adding fine zinc dust. Electrolysis of the purified zinc sulfate solution results in the formation of metallic zinc [4]. The overall reaction is:

$$ZnSO_4 + H_2O \rightarrow Zn + H_2SO_4 + 0.5O_2. \tag{3}$$

Cell voltage varies from 3.3 to 3.5 V/cell, while current efficiency ranges from 88% to 92%. Zinc deposition requires about 3100 kWh/mt, of which around one-third is converted to heat. Thus, the electrolyte has to be cooled to maintain an optimum bath temperature of 303–313 K [26].

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[1] Only 6% of the 2.245 kg sulfuric acid that are produced per kg of zinc is recycled to the process; 94% is excess sulfuric acid and considered as a commodity by-product. The avoided GHG emissions that result by displacing the conventional H_2SO_4 production by the on-site production are credited to the process.
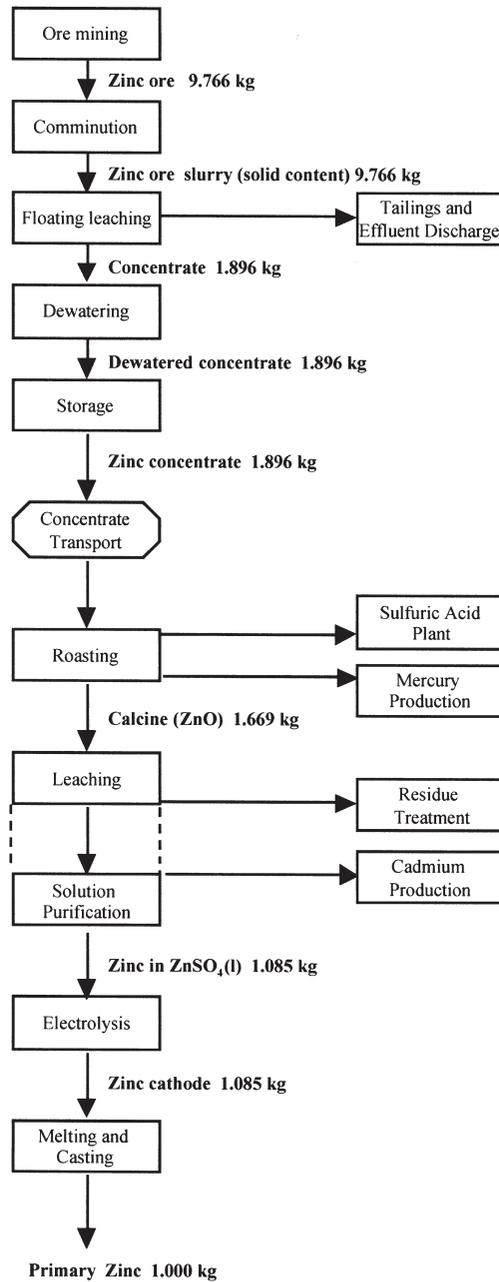
Fig. 1. Process chain for the conventional electrolytic production of zinc. Mass balance is normalized for the production of 1 kg primary zinc [4].

The sheet-like product obtained by stripping the cathode has a zinc content of at least 98.5%. It is washed, dried, and then smelted in low-frequency induction furnaces to receive high-grade molten zinc (>99.995%) that is cast in ingots. Power consumption is about 100–120 kWh/mt of zinc cast.

2.3. Conventional production of syngas — overview

The classical steam reforming of natural gas has been chosen in this study as the conventional route because it is the predominant process route for medium-sized syngas plants [3,21]. Fig. 2 shows the process chain. Mass balance is normalized for the production of 0.527 kg of syngas with a H_2/CO molar ratio of 2. The starting point is the extraction of natural gas (on- or offshore), followed by an on-site refining before being transported to the syngas processing plant. A rep-
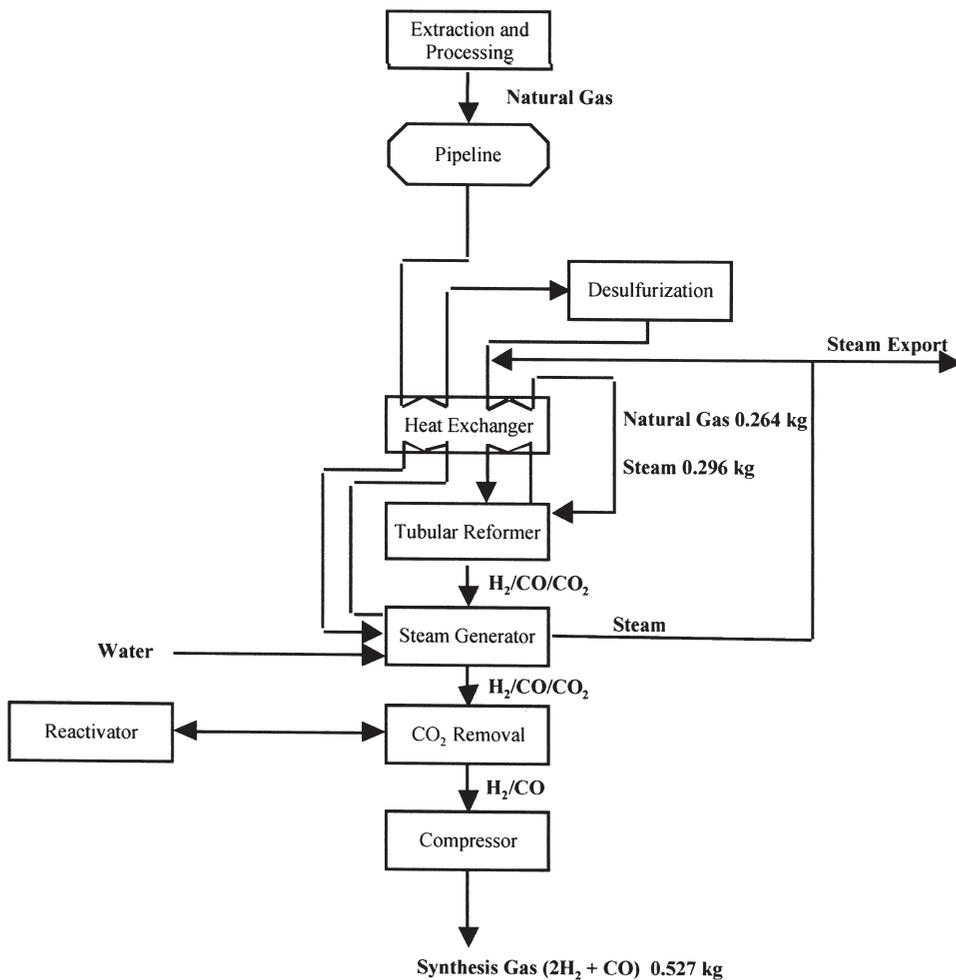

Fig. 2.   Process chain for the conventional syngas production by catalytic steam reforming of natural gas. Mass balance is normalized for the production of 0.527 kg syngas with a H_2/CO molar ratio of 2.

resentative natural gas composition for Europe, with low sulfur content, is assumed [20]. The module "Pipeline" is based on the main natural gas transportation pipeline between the Netherlands and Italy, which has 0.95 m diameter and 10 mm thickness, and uses about 240 mt of steel per km. Also accounted for are materials and energy consumption due to natural gas seasonal storage [20]. At the processing plant, a desulfurization stage precedes the reformer stage to avoid poisoning the nickel-based catalyst used in the steam reforming. Natural gas leaving the desulfurization tank is mixed with process steam, pre-heated to 800 K, and injected into a natural-gas-fired tubular reformer operated above about 1200 K [21,27]. A reformer contains several hundred tubes, 7–16 cm diameter, 0.5–2 cm thickness, 6–12 m length, made of nickel–chromium steel alloy. In the reformer, natural gas is steam-reformed according to:

$$CH_4 + H_2O \rightarrow CO + 3H_2. \tag{4}$$

The Boudouard equilibrium ($2CO \leftrightarrow CO_2 + C$), which leads to carbon deposits, can be prevented by using excess steam and avoiding long residence times in the critical temperature range 973–1073 K. The H_2 to CO ratio can be adjusted by help of the water-gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2. \tag{5}$$

The gas leaving the tubular reformer is cooled in heat exchangers which pre-heat the incoming natural gas stream and produce the steam required. Afterwards, the gas is led to the CO_2 removal unit by chemical absorption [21,28]. The CO_2-rich solvent is then regenerated by steam stripping and the CO_2 is recycled to the reformer. Optimal temperature and pressure conditions, along with CO_2 recycling and the water-gas shift reaction, lead to the desired H_2/CO ratio in the syngas[2] [21].

2.4. The SynMet solar co-production of zinc and syngas — overview

Fig. 3 shows the process chain. System boundaries are equivalent to those for the conventional routes of zinc and syngas production. Thus, the process chain starts with the mining of zinc ore and the extraction of natural gas. The final products are zinc ingots of equivalent purity (99.995%) and syngas of equivalent quality (H_2/CO molar ratio of 2). Mass and energy balances are normalized for the production of 1 kg of zinc and 0.527 kg of syngas. The reactants to the solar reactor are natural gas and ZnO calcine, obtained using the same operational modules of Figs. 1 and 2 as for the conventional productions. Newly added modules are the "Heliostat", the "Solar reactor", the "Refinery" and the "Compressor" units. A conceptual design of a large-scale solar SynMet plant is given in the following paragraphs. The solar collection plant is assumed to be a "tower reflector" central receiver plant of the type being developed at The Weizmann Institute of Science [23]. The optical configuration, called Cassegrain, is depicted in Fig. 4. It comprises a field of heliostats that collect and concentrate the sun rays on to a hyperboloid reflector installed on top of a tower. The upper hyperboloid's focus coincides with the heliostat field's aim point while the second focus coincides with the entrance plane of a compound parabolic concentrator (CPC) [29], used to augment the flux concentration ratio. With this arrangement, concentrated

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[2] Final purification and separation of CO and H_2 takes place in membrane units, cryogenic cold boxes and/or PSA (Pressure Swing Absorption) units [21]. This final separation has been omitted from consideration because it is not included in the process chain of Fig. 2.
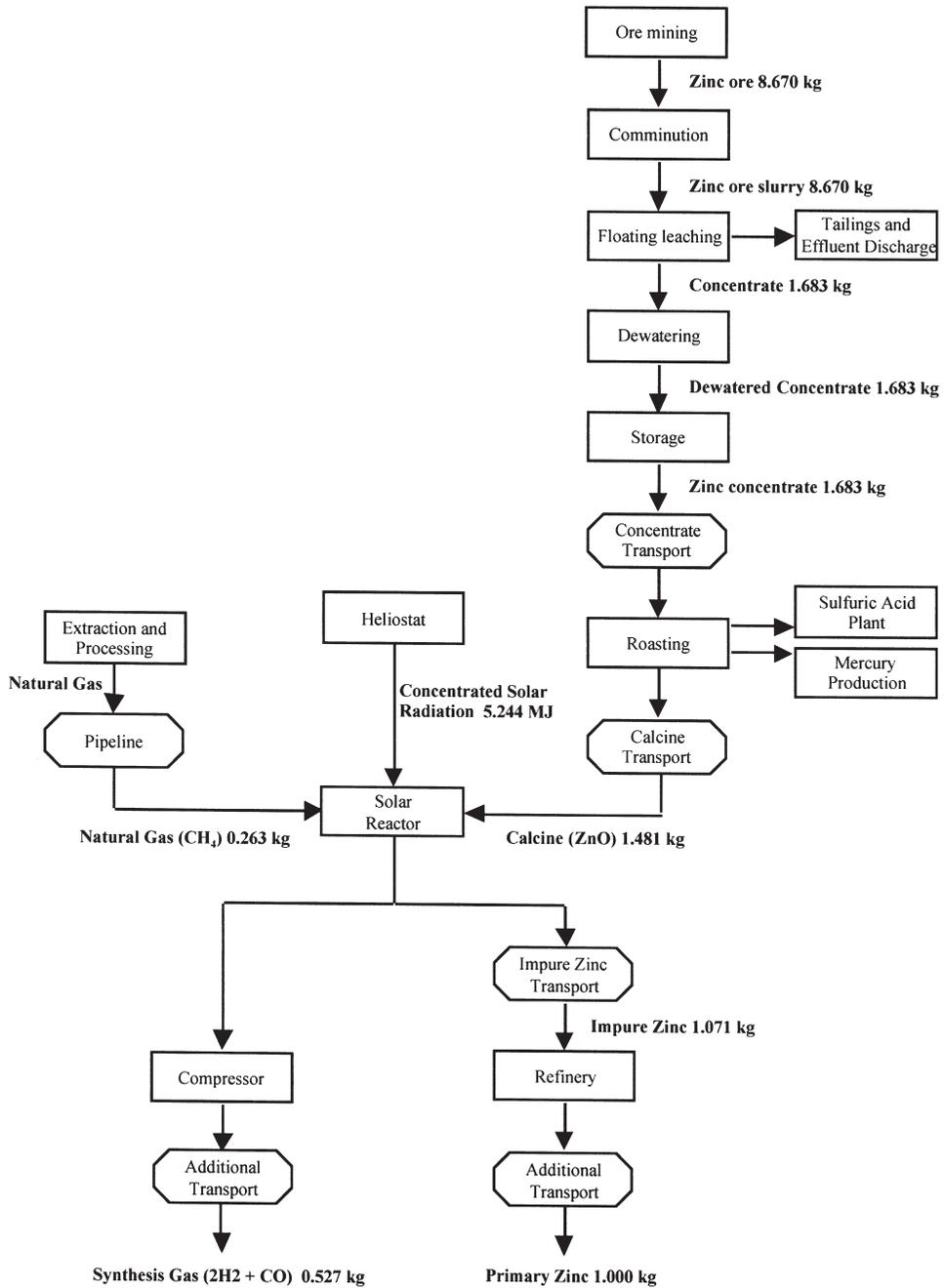
Fig. 3. Process chain for the solar co-production of zinc and syngas. Mass balance is normalized for the production of 1 kg primary zinc and 0.527 kg syngas with a H_2/CO molar ratio of 2.
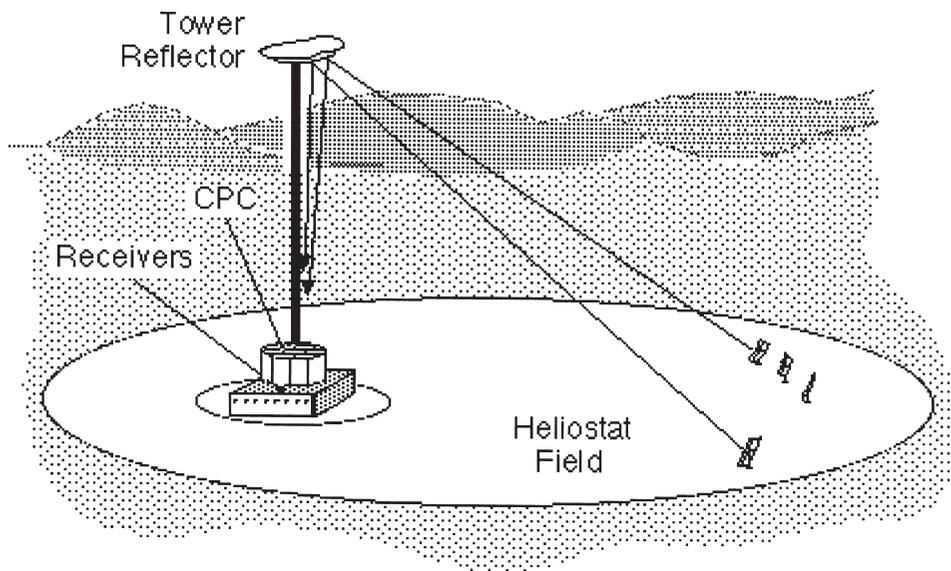
Fig. 4. Solar "tower reflector" central receiver plant concept, being developed at The Weizmann Institute of Science [23].

solar radiation emerging out of the CPC (or an array of CPCs) can enter the solar reactor (or an array of solar reactors) located on the ground level, eliminating the need for massive and expensive tower, piping and frequent personnel access to the tower top. The tower is only supporting a passive reflector component, whose area is typically about 2% of the heliostat field's area [23]. Assumed baseline parameters are: beam radiation of 2300 kWh/m^2/yr, 2300 equivalent full power hours per year, 60.4% annual optical efficiency (heliostat, tower reflector, CPC, radiation spillage) [30,31], 49% overall annual thermal annual efficiency,[3] mean flux solar concentration after CPC unit of 5000 kW/m^2. For the given baseline parameters, both material and energy flows through the system as well as the size of the heliostat field and tower reflector are calculated and summarized in Table 3.

An equimolar mixture of ZnO(s) and natural gas is fed into the solar reactor at 298 K and 1 atm. The reactants are pre-heated in an adiabatic counter-current-flow heat exchanger where a portion of the sensible and latent heat of the products is transferred to the reactants. After being pre-heated, the reactants enter the solar reactor and are further heated to the reactor temperature of 1250 K. Chemical equilibrium composition is assumed inside the reactor. Without heat recovery, the enthalpy change is 549 kJ/mol. The maximum possible heat recovery is 225 kJ/mol, reducing the solar requirement to 324 kJ/mol. After leaving the heat exchanger, the products are cooled rapidly to ambient temperature. Quenching is an irreversible step causing a significant drop in

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[3] Annual solar thermal efficiency is defined as the fraction of annual solar radiation used for process heat. It is calculated, on a yearly basis, as the ratio of the enthalpy change of the reaction to the solar beam radiation incident over the heliostat area. A reference solar plant of the same optical configuration with a 49% annual thermal efficiency has been chosen by The Weizmann Institute of Science to supply solar thermal energy to a 34 MW$_e$ net gas turbine combined cycle power station [30,31]. It is assumed that an analogous optical system can deliver the same energy to a chemical reactor at 1300 K.

Table 3
Material and energy flows for an industrial-sized SynMet solar chemical plant

Zinc metal production (mt/yr)	50,000
Synthesis gas production (mt/yr)	24,615
Solar input/year (MWh/yr)	69,231
Solar power capacity (MW)	30
Design ZnO feed (mt/h)	32.2
Design natural gas feed (mt/h)	5.7
Heliostat area (m^2)	62,709
Tower reflector area (m^2)	1254

the energy conversion efficiency. For the case of maximum heat recovery, the heat lost by quench-ing is 12 kJ/mol; without heat recovery, it is 237 kJ/mol. The separation of Zn(s) and syngas is accomplished naturally, without expenditure of work.[4] While syngas has the desired quality, zinc undergoes an additional refining step for obtaining the desired purity. Syngas also undergoes compression to 70 atm for pipeline transportation. Table 4 summarizes the enthalpy changes for the solar process without heat recovery under steady-state operating conditions [12]. Parasitic energy investment in startup/shutdown transients is assumed to be negligible for directly irradiated solar reactors because of their low thermal inertia and efficient heat transfer [11].

For all the three processes, the plant's life is presumed to be 30 years. Considered in the Life Cycle Assessment are also waste materials derived from any of the processes and their infrastruc-tures that are either sent to an inert material disposal (e.g., glass and concrete) or to a regular waste incineration plant (e.g., organic materials).

Table 4
Standard enthalpy changes for effecting: ZnO(s)+CH$_4$ @ 300 K→Zn(s)+2H$_2$+CO @ 300 K

Step	T (K)	$\Delta H°$ (kJ/mol)
Heat ZnO	300 to 1250	+48
Heat CH$_4$	300 to 1250	+58.5
ZnO+CH$_4$→Zn(g)+2H$_2$+CO	1250	+442
Cool Zn(g)+2H$_2$+CO	1250 to 300	−237
Zn(g)→Zn(l)	–	−116
Zn(l)→Zn(s)	693	−7

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[4] The quenching and separation of zinc vapor may require the use of lead-spray condensers which are commonly employed in carbothermic Imperial smelting furnaces, or the development of energy-efficient units for the complete heat recovery and separation of zinc. In this study it is assumed that the cooling and separation of the chemical products are accomplished in a counter-current-flow heat exchanger coupled to an electrostatic filter, and that these units are part of the "Solar reactor" module of Fig. 3.

Table 5
Accumulated emissions of CO_2, CH_4, N_2O and CO_{2-eq} for each module of the process chain of the conventional electrolytic production of 1 kg primary zinc. Units are kg/kg of Zn

	CO_2	CH_4	N_2O	CO_{2-eq}
Ore mining	1.52×10^{-1}	2.76×10^{-4}	2.05×10^{-6}	1.58×10^{-1}
Comminution	1.57×10^{-1}	3.45×10^{-4}	8.13×10^{-6}	1.66×10^{-1}
Floating leaching	2.29×10^{-1}	4.46×10^{-4}	1.86×10^{-6}	2.39×10^{-1}
Dewatering	9.27×10^{-2}	1.13×10^{-4}	2.90×10^{-6}	9.63×10^{-2}
Storage	4.26×10^{-3}	8.33×10^{-6}	3.45×10^{-8}	4.45×10^{-3}
Concentrate transport	1.03×10^{-1}	1.69×10^{-4}	2.16×10^{-6}	1.07×10^{-1}
Roasting	9.16×10^{-2}	1.72×10^{-4}	7.81×10^{-7}	9.55×10^{-2}
Leaching and purification	1.06×10^{-1}	2.23×10^{-4}	1.38×10^{-6}	1.11×10^{-1}
Electrolysis	1.93×10^{0}	3.66×10^{-3}	1.56×10^{-5}	2.01×10^{0}
Smelting and casting	1.46×10^{-1}	2.95×10^{-4}	2.89×10^{-6}	1.53×10^{-1}
Sulfuric acid production	2.63×10^{-1}	4.92×10^{-4}	8.26×10^{-6}	2.76×10^{-1}
Infrastructure	1.00×10^{-1}	1.92×10^{-4}	1.77×10^{-6}	1.05×10^{-1}
Credits	-3.63×10^{-1}	-7.99×10^{-4}	9.24×10^{-6}	3.83×10^{-1}
Total	3.01×10^{0}	5.60×10^{-3}	3.85×10^{-5}	3.14

3. Results — environmental impact assessment

Tables 5–7 show the results of the Life Cycle Assessment for the conventional zinc production, the conventional syngas production and the solar co-production of zinc and syngas, respectively. Listed are the accumulated CO_2, CH_4, N_2O, and CO_2-equivalents for each process step, for the transport, and for the infrastructure, and finally for the sum of emissions over the entire process chain. The emissions avoided that result by displacing the conventional sulfuric acid production by the on-site production are credited to the processes.

Total emissions for the conventional electrolytic production of zinc from its ore are 3.14 CO_{2-eq} per kg zinc (99.995% purity). Total emissions for the conventional production of syngas by catalytic steam reforming of natural gas are 0.55 CO_{2-eq} per 0.527 kg syngas (molar ratio $H_2/CO=2$ for quality). Total emissions for the SynMet solar co-production of zinc and syngas are 1.51 CO_{2-eq} per 1 kg zinc and 0.527 kg syngas. Thus, the SynMet process offers the potential of reducing CO_{2-eq} emissions by 59%.

Table 6
Accumulated emissions of CO_2, CH_4, N_2O and CO_{2-eq} for each module of the process chain of the conventional production of 0.527 kg syngas by catalytic steam reforming of natural gas. Units are kg/0.527 kg syngas

	CO_2	CH_4	N_2O	CO_{2-eq}
Extraction/processing	2.14×10^{-2}	4.31×10^{-4}	4.73×10^{-7}	3.06×10^{-2}
Pipeline transport	2.99×10^{-3}	1.01×10^{-5}	5.14×10^{-8}	3.22×10^{-3}
Steam reforming	4.41×10^{-1}	1.11×10^{-3}	2.09×10^{-6}	4.65×10^{-1}
Infrastructure	4.84×10^{-2}	2.20×10^{-4}	6.78×10^{-7}	5.32×10^{-2}
Total	5.14×10^{-1}	1.77×10^{-3}	3.29×10^{-6}	0.55

Table 7

Accumulated emissions of CO_2, CH_4, N_2O and $CO_{2\text{-eq}}$ for each module of the process chain of the SynMet solar thermal co-production of 1 kg primary zinc and 0.527 kg syngas. Units are kg/kg Zn and 0.527 kg syngas

	CO_2	CH_4	N_2O	$CO_{2\text{-eq}}$
Extraction and processing	2.66×10^{-2}	4.71×10^{-4}	3.33×10^{-7}	3.66×10^{-2}
Pipeline transport	1.50×10^{-3}	5.17×10^{-6}	2.53×10^{-8}	1.62×10^{-3}
Ore mining	1.35×10^{-1}	2.45×10^{-4}	1.82×10^{-6}	1.40×10^{-1}
Comminution	1.39×10^{-1}	3.06×10^{-4}	7.22×10^{-6}	1.48×10^{-1}
Floating leaching	2.03×10^{-1}	3.96×10^{-4}	1.65×10^{-6}	2.12×10^{-1}
Dewatering	8.23×10^{-2}	1.16×10^{-4}	2.58×10^{-6}	8.55×10^{-2}
Storage	3.78×10^{-3}	7.39×10^{-6}	3.06×10^{-8}	3.95×10^{-3}
Concentrate transport	9.10×10^{-2}	$1.50 \times 1^{0-4}$	1.92×10^{-6}	9.48×10^{-2}
Roasting	8.13×10^{-2}	1.53×10^{-4}	6.93×10^{-7}	8.48×10^{-2}
Calcine transport	5.28×10^{-2}	9.50×10^{-5}	1.54×10^{-6}	5.53×10^{-2}
Heliostat	2.58×10^{-3}	4.89×10^{-6}	2.03×10^{-8}	2.69×10^{-3}
Reactor	5.47×10^{-3}	1.13×10^{-5}	3.94×10^{-7}	5.83×10^{-3}
Compressor	5.91×10^{-2}	1.12×10^{-4}	4.65×10^{-7}	6.16×10^{-2}
Impure zinc transport	2.90×10^{-2}	5.63×10^{-5}	1.06×10^{-6}	3.05×10^{-2}
Refinery	5.57×10^{-1}	1.39×10^{-3}	4.03×10^{-6}	5.88×10^{-1}
Additional transport	5.44×10^{-2}	9.79×10^{-5}	1.59×10^{-6}	5.70×10^{-2}
Sulfuric acid production	2.34×10^{-1}	4.37×10^{-4}	7.33×10^{-6}	2.45×10^{-1}
Infrastructure	1.00×10^{-2}	2.82×10^{-5}	2.37×10^{-5}	1.80×10^{-2}
Credits	-3.43×10^{-1}	-7.55×10^{-4}	-8.72×10^{-6}	-3.62×10^{-1}
Total	1.42×10^{0}	3.33×10^{-3}	4.77×10^{-5}	1.51

Table 5 indicates that the major contribution to the GHG output for the conventional zinc production is coming from the electrolysis step, amounting to 64% of the total emissions and derived mainly from the high electricity consumption. Table 6 indicates that, for the conventional syngas production, the major $CO_{2\text{-eq}}$ contribution is coming from the natural gas combustion during the reforming step, amounting to 84% of the total emissions. As far as the solar process is concerned, the $CO_{2\text{-eq}}$ emissions derived from the solar-related modules "Heliostat" and "Solar reactor" are negligible. Major contributions are coming from the conventional pre- and post-processing of the material (78% of total), such as the "Floating leaching" module (14% of total) and the "Refinery" module (39% of total). Another important emission source appears to be transportation; when all transport distances are summed up, transportation is responsible for 16% of the total $CO_{2\text{-eq}}$ emissions.

GHG emissions can be reduced further by using recycled ZnO as raw material instead of the zinc ore because the recovery of zinc from waste materials (e.g., metallurgical scrap, discharged batteries and galvanized steel) is less energy-intensive. Zinc is completely recyclable without any loss of its physical or chemical properties. At present, 36% of the world's zinc supply comes from recycled zinc [2]. When ZnO is recycled, all the modules preceding "Leaching" in the process chain of Fig. 1 and all the modules preceding "Calcine transport" in the process chain of Fig. 3 are omitted. Also omitted is any credit for the on-site production of sulfuric acid. Thus, when ZnO is recycled, total emissions for conventional electrolytic zinc production are 2.66

$CO_{2\text{-eq}}$ per kg zinc, while total emissions for the SynMet solar co-production of zinc and syngas are 0.86 $CO_{2\text{-eq}}$ per 1 kg zinc and 0.527 kg syngas.

4. Summary and conclusions

A Life Cycle Assessment has been conducted for the conventional electrolytic production of zinc, for the conventional production of syngas by catalytic steam reforming of natural gas, and for the solar co-production of zinc and syngas by the SynMet process. The assessment includes determination of the materials and energy expenses caused by each process step, infrastructure and transportation. An electricity mix with a 14.8% share of renewables (including hydro) was adopted for this study [25]. Total emissions for the conventional zinc production are 3.14 $CO_{2\text{-eq}}$ per kg zinc (99.995% purity). Total emissions for the conventional syngas production are 1.04 $CO_{2\text{-eq}}$ per kg syngas (molar ratio $H_2/CO=2$ for quality). Total emissions for the SynMet solar co-production of zinc and syngas are 1.51 $CO_{2\text{-eq}}$ per 1 kg zinc and 0.527 kg syngas. Thus, replacing the conventional fossil-fuel-based processes by a solar combined process results in a $CO_{2\text{-eq}}$ emission reduction of 59%. For the conventional zinc production, main emission sources are derived from the electricity consumption in the electrolytic step and represent 64% of the total emissions. For the conventional syngas production, main emission sources are derived from the combustion of fossil fuels in the endothermic steam-reforming step and represent 85% of the total emissions. For the solar production, main emission sources are derived from process steps during the pre- and post-processing of materials (78% of total emissions), and from their transportation to/from the solar site (16% of total emissions). However, $CO_{2\text{-eq}}$ emissions derived from the solar processing step and its infrastructure are negligible.

The accuracy of this Life Cycle Assessment is limited principally by the accuracy of the assumptions for the SynMet process because of its early stage of development. The technical feasibility of an industrial-scale SynMet plant needs demonstration. The beam-down solar tower system also needs demonstration but an alternative solar plant configuration with receivers in the tower could be developed.

Acknowledgements

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