Environmental life cycle assessment of cemented carbide (WC-Co) production

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A B S T R A C T

Cemented carbides are of great importance for the manufacturing industry. The outstanding properties of high hardness and wear resistance of this material, consisting mainly of tungsten carbide cemented with cobalt (WC-Co), have caused its use in a wide range of applications. The aim of this study is to provide comprehensive and detailed cradle-to-gate life cycle inventory (LCI) data for the typical non-Chinese production of WC-Co, which is assumed to take place in Canada and the United States. Different scenarios are presented regarding recycling rate and a life cycle impact assessment (LCIA) is conducted to illustrate the applicability of the LCI data. The LCI results in this study are of similar magnitude or lower compared to previous studies and indicate that the typical non-Chinese production requires less energy compared to Chinese production. The LCIA results show that the mining, hydro-metallurgy and powder metallurgy phases in general dominate the cradle-to-gate life cycle impacts. Most of the impacts are caused by a limited number of inputs and outputs (e.g. kerosene, sulfidic tailings, water use during mining and electricity use), and recycling greatly reduces the impacts. A comparison with Chinese tungsten carbide (WC) powder production showed that the LCIA results in non-Chinese WC production were lower for climate change, photochemical oxidant formation and water depletion, but higher for terrestrial acidification, ozone depletion and freshwater eutrophication. The LCI data and the LCIA results for non-Chinese production can subsequently be used in product-specific cradle-to-grave life cycle assessments involving WC-Co or any of its precursors.

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1. Introduction

The outstanding properties of cemented carbides, including high hardness and wear resistance, have caused this material to be used in a wide range of applications, especially in rock drilling tools as well as cutting tools for metals, plastics, wood and composites in the manufacturing industry (Fang et al., 2014). Cemented carbides consist mainly of tungsten carbide cemented with cobalt (WC-Co) (Prakash, 2014). To date, only a few sources of life cycle inventory (LCI) data for WC-Co and its precursors exist. The recent paper by Ma et al. (2017) reported LCI data for the production of tungsten carbide (WC) powder, a precursor to WC-Co, for two production sites in China. The global tungsten mine production is indeed dominated by China at about 80%. However, less than half of the global production of cemented carbides occur in China and only 23% of that was exported in 2015 (Hu et al., 2016; Leal-Ayala et al.,

2015). There is thus also a need for LCI data representing non-Chinese WC-Co production.

Some previous studies have attempted to compile LCI data for non-Chinese production of WC-Co or one of its precursors. The PROBAS database contains LCI data for tungsten metal, but that data is rough estimations based on copper production that do not include direct emissions or resource use from the foreground system (e.g. mining) (PROBAS, 2000). LCI data for the production of the precursor tungsten trioxide (WO_3) was provided by Syrrakou et al. (2005). Only input materials were considered in that study, whereas energy requirement, emissions and waste were not. Xiong et al. (2008) provided laboratory-scale data for two production routes of WC-Co, which only cover some life-cycle processes. Studies conducting life cycle assessment (LCA) of tungsten-containing products largely obtained LCI data from Syrrakou et al. (2005), see for example Bobba et al. (2016) and Wigger et al. (2017). Recycling processes were not considered in any of the above-mentioned LCI data sets, despite tungsten being recycled at 10–25% after use globally (Graedel et al., 2011).

The aim of this study is to provide comprehensive and detailed LCI data for typical non-Chinese production of WC-Co from cradle to gate for different recycling scenarios. This study thus complements Ma et al. (2017) by considering production of WC-Co outside China. A life cycle impact assessment (LCIA) is conducted to illustrate the applicability of the LCI data and to identify environmental hotspots. Both the LCI data and the LCIA results can be subsequently used by LCA practitioners in product-specific cradle-to-grave LCAs involving WC-Co. The LCI data can furthermore be used in LCAs of any of the WC-Co precursors.

2. Material and methods

LCA is the most well-developed tool for environmental assessment of products (Ness et al., 2007). This study is a cradle-to-gate LCA, thus including the life cycle phases from the extraction of raw materials to the production of the WC-Co (Baumann and Tillman, 2004). It is furthermore an attributional study, meaning that the environmental impacts associated with the product system are assessed, rather than environmental impacts of changes in product systems (Finnveden et al., 2009). However, the LCI data derived can also be used in consequential studies of environmental impacts related to WC-Co-containing products. The study is conducted in accordance with the ISO 14040 standard (ISO, 2006).

2.1. Functional unit

Mechanical properties of WC-Co depend on the cobalt content and the WC grain size, which can be adjusted to reach desirable properties for specific applications (Lassner and Schubert, 1999). An increase in cobalt content results in lower hardness but higher toughness, while the opposite applies for grain size. The cobalt content of commercial WC-Co therefore varies for different applications, with 6–16% being common, and the WC grain size used for producing WC-Co typically varies from 0.2 to tens of microns (Fang et al., 2014). The functional unit was thus set to 1 kg of WC-Co, with a cobalt content of 6–16% and WC grain size >0.2 μm. This corresponds, in the case of 6% cobalt, to tools requiring high hardness, used for e.g. metal cutting, mining and wood working (Prakash, 2014). In the case of 16% cobalt, it corresponds to tools requiring high toughness, e.g. for cold forming and hot rolling (Prakash, 2014).

2.2. System studied

The studied production system represents the typical non-Chinese production of WC-Co (Fig. 1). A major difference between Chinese and non-Chinese WC production is that the former uses solid ion-exchange technology whereas the latter mainly uses solvent extraction for the removal of impurities in tungsten ores (Wolfe et al., 2014). The typical production here represents the technology that is commonly used in non-Chinese WC-Co production, which is described in more detail in Section 3. In this way, the typical non-Chinese WC-Co production represents the general technology applied to produce WC-Co outside China. A distinction between the foreground system and background system is made (Tillman, 2000), where the former contains the production of tungsten concentrates, ammonium paratungstate (APT), WC powder and WC-Co, and the latter contains the production of input materials, energy and waste management. The production of WC-Co from tungsten concentrates was assumed to take place in the United States (US), where most major tungsten powder and WC processing plants are located (Werner et al., 2014). Production of tungsten concentrates is often situated at the mine site to reduce transportation costs (Lassner and Schubert, 1999), thus the mining

of tungsten and the production of tungsten concentrates were assumed to take place in Canada, which is a main supplier of tungsten to the US (USGS, 2016, 2018). Environmental impacts of capital goods are not included. The cut-off method was used for allocation in waste treatment, meaning that each recycled product is responsible for its direct impacts only (Ekvall and Tillman, 1997).

### 2.3. Impact categories and impact assessment methods

An impact assessment was conducted in order to illustrate how the LCI data can be applied and to identify environmental hotspots. The impact categories of global warming potential, acidification potential, eutrophication potential, smog potential, ozone depletion potential, net water consumption, primary energy requirement (total, fossil and renewable) and waste generation were included as recommended by Santero and Hendry (2016) for LCAs of metals. The impact assessment method suite ReCiPe (version 2008) with the hierarchist scenario (Goedkoop et al., 2013) was applied for most impact categories (Table 1). This version, and not the latest method suite ReCiPe (version 2016) (Huijbregts et al., 2017), was applied in order to maintain compatibility with the Ecoinvent database (2017) that was used for the background system LCIA data (Section 2.4). However, since ReCiPe does not include impact categories for primary energy requirement and waste generation, the cumulative energy demand (CED) (Frischknecht et al., 2015) and EDIP2003 methods (Wenzel et al., 1998) were instead used for these purposes, respectively.

2.4. Impact assessment data

For the LCIA, background system data for the selected impact categories (Section 2.3), was mainly obtained from the Ecoinvent database (2017) version 3.4, applying the "allocation, cut-off by classification" system model. When available, site-specific data was applied, otherwise global data or in second-hand "rest-of-the-world" data, representing global data excluding Europe, was used. Site-specific data were only available for electricity, which was modelled based on the location of its use (i.e. Canada and the US). If data for a product in the background system was unavailable in the Ecoinvent database (2017), data for similar products were used when possible, e.g. decanol was modelled using data for fatty alcohol, or a literature search for LCI or LCIA data was conducted. The sources of the background system data are presented in Section S2 in the Supplementary material (SM). The contribution from direct emissions in the foreground system of carbon dioxide (CO_2), ammonia (NH_3), heptane (C_7H_{16}), hexane (C_6H_{14}) and paraffin to their respective environmental impacts was estimated based on Goedkoop et al. (2013) and all solid waste was added to the landfilling of the background system.

2.5. Uncertainty and sensitivity analysis

In order to assess uncertainty, scenario analysis was applied. Model uncertainty was handled by constructing five different scenarios by varying the recycling rate and the type of tungsten ore (Table 2). The typical non-Chinese production scenario constitutes a basis from which all other scenarios were constructed. The global recycling rate of tungsten is about 10–25% (Graedel et al., 2011) and the midpoint value of 17% was applied in this scenario. In the zero-recycling scenario, no recycling occurs, while in the complete recycling scenario, all tungsten input originates from recycled materials. Scheelite and wolframite are the only tungsten ores of industrial importance. In the scheelite ore scenario, only scheelite ore is assumed, whereas only wolframite ore is assumed in the wolframite ore scenario. In all other scenarios, we assume the

CaWO4 ore   (Fe,Mn)WO4 ore

Mining

Extraction, crushing and milling   Extraction, crushing and milling

Energy →

Milled CaWO4 ore   Milled (Fe,Mn)WO4 ore

H_2O → Gravity methods and grinding → Gangue, W loss

H_2O → Gravity methods and grinding → Gangue, W loss

H_2O, anyl xanthate, Na_2S, pine oil → Sulfide flotation

Low concentration fraction

High concentration fraction → Scheelite flotation

Na_2CO_3, Na_2SiO_3, tannin, NaCN, $C_{18}H_{34}O_2$, frother →

→ Gangue, W loss, Na_2S, anyl xanthate, Na_2CO_3, Na_2SiO_3, tannin, NaCN, frother

Roasting → CO_2

CaWO4 concentrates   (Fe,Mn)WO4 concentrates

Transport

Hydrometallurgy

Na_2CO_3, H_2O → Na_2CO_3 Digestion

NaOH, H_2O → NaOH Digestion

Energy, W scrap, NaOH → Chemical recycling

Impure Na_2WO_4 solution

Filtration

→ Undissolved gangue, W lost and insoluble reaction compounds (from filtration)
Precipitates containing impurities (from Si and Mo precipitation)
Insoluble metal oxides (from chemical recycling)

Energy →

Purer Na_2WO_4 solution

$Al_2(SO_4)_3 \cdot 18H_2O$, $MgSO_4 \cdot 7H_2O$ → Si precipitation

Even purer Na_2WO_4 solution → CO_2 (for scheelite)

NaHS, H_2SO_4, wash H_2O → Mo precipitation → MoS_3, H_2S, wash H_2O

Purified Na_2WO_4 solution

Organic solvent (alamine 336, decanol, kerosene), H_2SO_4, deionized H_2O, NH_3, H_2O → Solvent extraction → Na_2SO_4, deionized H_2O, organic solvent (alamine 336, decanol, kerosene), NH_3

$(NH_4)_2WO_4$ solution

Crystallization → NH_3

APT

Pyrometallurgy

Energy → Calcination → NH_3

TBO

H_2 → H_2 reduction → H_2

W metal powder

Carbon black, H_2 → Carburization → H_2, CO_2

WC powder

Powder metallurgy

Co powder, organic solvent (C_7H_{16} or C_6H_{14}), paraffin, Energy, WC-Co scrap, Zn → Zn recycling

WC, Co powder → Powder milling → Organic solvent (C_7H_{16} or C_6H_{14})

Slurry

→ WC-Co loss, Zn

N_2 → Granulation and compaction → Organic solvent (C_7H_{16} or C_6H_{14}), N_2, un-granulated powder and paraffin

Energy →

Compacted part

Sintering → Paraffin

FOREGROUND SYSTEM
BACKGROUND SYSTEM

WC-Co

Legend:
- - - System boundary
▢ Phase
▢ Process
→ Main product flow
→ Inputs and outputs

Fig. 1. Flowchart for the typical non-Chinese tungsten carbide with cobalt (WC-Co) production. $CaWO_4$ = scheelite, $(Fe,Mn)WO_4$ = wolframite, H_2O = water, W = tungsten, Na_2S = sodium sulfide, Na_2CO_3 = sodium carbonate or soda ash, Na_2SiO_3 = sodium silicate, NaCN = sodium cyanide, $C_{18}H_{34}O_2$ = oleic acid, CO_2 = carbon dioxide, NaOH = sodium hydroxide, Na_2WO_4 = sodium tungstate, $Al_2(SO_4)_3 \cdot 18H_2O$ = aluminum sulfate solution, $MgSO_4 \cdot 7H_2O$ = magnesium sulfate solution, Si = silica, Mo = molybdenum, NaHS = sodium hydrosulfide, H_2SO_4 = sulfuric acid, MoS_3 = molybdenum trisulfide, H_2S = hydrogen sulfide, NH_3 = ammonia, Na_2SO_4 = sodium sulfate, $(NH_4)_2WO_4$ = ammonium tungstate, ammonium paratungstate (APT), tungsten blue oxide (TBO), H_2 = hydrogen, WC = tungsten carbide, Co = cobalt, C_7H_{16} = heptane, C_6H_{14} = hexane, Zn = zinc and N_2 = nitrogen.

tungsten content originate from 75% scheelite and 25% wolframite ore based on their shares in existing tungsten deposits (Lassner et al., 2000). Parameter uncertainty in the foreground system was handled by constructing a baseline case, as well as low and high environmental impact cases (abbreviated BC, LC and HC, respectively). Whenever input data ranges were available, the value resulting in highest impacts was applied for the HC, the value resulting in lowest impacts was applied for the LC, and the midpoint value was applied in the BC.

A sensitivity analysis was furthermore conducted by varying one parameter at a time while investigating the resulting variations in the impact assessment results relative to the BC for the typical non-Chinese production of WC-Co. Parameters were varied using the LC and HC values when available following Igos et al. (2018), who recommend to preferably apply realistic ranges for parameters in sensitivity analysis. When no information on ranges was available, parameters were changed by ±50% of its value in the BC in order to get an indication on which of these parameters that are of specific interest for further investigations. The parameter values applied in the sensitivity analysis are provided in Section S1 in the SM.

3. Calculations

Data was collected from an extensive literature and database search and was chosen to illustrate the typical non-Chinese production of WC-Co. Tungsten losses are minimal in many of the process steps (Lassner and Schubert, 1999; Leal-Ayala et al., 2015; Upadhyaya, 1998; Yih and Wang, 1979) and yields were thus for simplification purposes assumed to be effectively 100% unless otherwise noted in Sections 3.1-3.6. The data applied for the LCI calculations are presented in Sections 3.1-3.6 and summarized in Section S1 in the SM.

3.1. Mining

Extraction of ore is done through drilling, blasting and digging, after which the ore is crushed and milled (Leal-Ayala et al., 2015). The energy required to produce scheelite concentrates has been estimated at 31.7 kWh electricity and diesel/ton ore (Leal-Ayala et al., 2015). In US metals mining, diesel is typically used in materials handling (46% of mining energy requirement), while diesel or electricity can be used in extraction and beneficiation (14% and 40% of mining energy requirement, respectively) (USDoE, 2007). In the LC, electricity was therefore assumed for both extraction and beneficiation, while diesel only was assumed in the HC. In the BC, half of the extraction plus beneficiation energy was assumed to be electricity and the rest diesel. The energy required to produce wolframite concentrates was assumed to be the same as for scheelite concentrates.

3.1.1. Gravity methods and grinding

The tungsten content is approximately 0.4—0.6% in workable ores (Lassner et al., 2000; Wolfe et al., 2014). In order to increase the concentration, gangue material, which is commercially unprofitable materials such as quartzite, silicates and sulfide ores (Lassner et al., 2000), has to be removed from the milled ore. Gravity methods are commonly applied for this purpose, where the milled ore is mixed with water (H_2O) and then cycloned (Lassner and Schubert, 1999; Wolfe et al., 2014). The H_2O input is 20—30% of the mixture (Yih and Wang, 1979) and the yield is 60—90% tungsten for scheelite ore (Lassner et al., 2000). This data was applied for wolframite ore as well due to limited information. The separated components from the gravity methods, i.e. gangue material and lost tungsten, constitute tailings. Tungsten ores can be sulfidic (Lassner et al., 2000) and since sulfidic tailings generally cause higher

emissions (Ecoinvent database, 2017), the LC assumes 0%, the HC 100% and the BC 50% sulfidic tailings.

Milled wolframite ore is then grinded, and the tungsten concentration of the output is 42—53%, most typically 52% (Wolfe et al., 2014), which was therefore applied in the BC instead of the midpoint value. The milled scheelite ore comes in a high and a low concentration fraction (56—58% (Wolfe et al., 2014) vs about 0.41% tungsten (Martins and Amarante, 2013), respectively), where only the high concentration fraction (60% tungsten by mass (Martins and Amarante, 2013; Yih and Wang, 1979)) requires grinding due to its coarser mineralization (Lassner, 1995). The low concentration fraction, constituting of finely mineralized scheelite which was rejected from gravity methods as tailings, is despite its low tungsten content relative the high concentration fraction further treated in order to improve the tungsten yield.

3.1.2. Sulfide and scheelite flotations

Both the high and low concentration fractions of milled scheelite ore undergo sulfide flotation to remove sulfides (Lassner and Schubert, 1999; Wolfe et al., 2014). The fractions are mixed with 60—65% H_2O (Martins and Amarante, 2013; Yih and Wang, 1979), and 20 g anyl xanthate (as collector), 500 g sodium sulfide (as regulator) as well as 4 g pine oil (as frother) are typically added per ton of slurry (Martins and Amarante, 2013). Collectors adsorb to particles targeted for recovery, regulators ensure that the collectors target the right particles and frothers enhance the recovery of these particles (Bulatovic, 2007). The output from sulfide flotation constitutes scheelite concentrates and pine oil frother, whereas other reagents and separated materials are removed as gangue (Wolfe et al., 2014). The high concentration fraction after sulfide flotation enters the roasting process directly, while the low concentration fraction first passes through scheelite flotation.

In the scheelite flotation process, additional collectors, regulators and frothers are added to the low concentration fraction, with typical inputs being 0.48—6.5 g sodium carbonate (Na_2CO_3), 1—3.75 g sodium silicate (Na_2SiO_3), 0.05—0.75 g tannin and 0.05—0.5 g sodium cyanide (NaCN) as regulators; 0.4—1 g oleic acid ($C_{18}H_{34}O_2$) as collector; and 0.025—0.09 g pine oil as frother per kg ore (Yih and Wang, 1979). The $C_{18}H_{34}O_2$ follows the low concentration fraction, while all the other reagents are separated (Bulatovic, 2007) together with the gangue and lost tungsten. The tungsten yield in the scheelite flotation process is 80—90% (Lassner et al., 2000).

Tailings from the sulfide and scheelite flotations were handled as described in Section 3.1.1 and calculated as the material lost (gangue and tungsten) when going from a tungsten concentration of about 0.41% in the low concentration fraction to 56—58% in concentrates (Martins and Amarante, 2013; Wolfe et al., 2014).

3.1.3. Roasting

Organics from the sulfide and scheelite flotation processes that accompany the scheelite concentrate need to be removed before further processing (Wolfe et al., 2014). Roasting is therefore applied, in which the pine oil (approximate chemical formula: $C_{11}H_{18}O$ (Toch, 1914)) from sulfide flotation and $C_{18}H_{34}O_2$ from scheelite flotation are eliminated by oxidation at about 540 °C:

$$C_{11}H_{18}O + 15O_2 \rightarrow 11CO_2 + 9H_2O \tag{R1}$$

$$C_{18}H_{34}O_2 + 25O_2 \rightarrow 18CO_2 + 16H_2O \tag{R2}$$
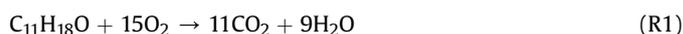
The output is a high-grade scheelite concentrate with a tungsten content of 56—58% as well as CO_2 emissions (Wolfe et al., 2014).

Table 1
Impact categories included, along with corresponding indicators applied in this study. CO_2 = carbon dioxide, SO_2 = sulphur dioxide, P = phosphorous, NMVOC = non-methane volatile organic compounds and CFC-11 = trichlorofluoromethane.

Impact category	Indicator	Reference
Global warming potential	Climate change [kg CO_2 eq]	Goedkoop et al. (2013)
Acidification potential	Terrestrial acidification [kg SO_2 eq]	
Eutrophication potential	Freshwater eutrophication [kg P eq]	
Smog potential	Photochemical oxidant formation [kg NMVOC eq]	
Ozone depletion potential	Ozone depletion [kg CFC-11 eq]	
Net water consumption	Water depletion [m^3]	
Primary energy requirement (total, fossil and renewable)	Cumulative energy demand (total, fossil and renewable) [MJ eq]	Frischknecht et al. (2015)
Waste generation	Land filling [kg waste]	Wenzel et al. (1998)

Table 2
Scenarios constructed by varying the recycling rate and the type of tungsten ore.

Scenario	Tungsten input		
	Recycling rate	Scheelite ore	Wolframite ore
Typical non-Chinese production	17%	62%	21%
Zero recycling	0%	75%	25%
Complete recycling	100%	0%	0%
Scheelite ore	17%	83%	0%
Wolframite ore	17%	0%	83%

3.2. Transport

The major Canadian tungsten deposits, for example the Cantung mine, are located in the Yukon and Northwest territories (Werner et al., 2014). The major WC-Co production plants are located in the eastern US, for example in Cleveland, Ohio (Werner et al., 2014). The road distance between the Cantung mine and Cleveland is about 5000 km, with truck being the likely mode of transport.

3.3. Hydrometallurgy

The energy required to produce 1 kg APT from concentrates is 1–1.6 kWh (EC, 2001; Wang et al., 1995). The materials removed during hydrometallurgy (undissolved gangue, insoluble reaction compounds, precipitates and lost tungsten) become solid waste and were calculated based on a mass balance over the entire hydrometallurgy phase excluding H_2O.

3.3.1. Sodium carbonate and hydroxide digestions with subsequent filtration

In the sodium carbonate digestion, scheelite concentrates are typically leached by a 10–18% Na_2CO_3 solution under pressure to obtain sodium tungstate (Na_2WO_4) (Lassner et al., 2000). This reaction requires a molar ratio of 2.5–4.5 between Na_2CO_3 and tungsten. In the sodium hydroxide digestion, wolframite concentrates are similarly leached by a 7–10% sodium hydroxide (NaOH) solution at a molar ratio of 1.05 between NaOH and tungsten (Lassner et al., 2000). The yield in sodium hydroxide digestion is 97–99% tungsten (Lassner and Schubert, 1999). Insoluble reaction compounds, tungsten lost and undissolved gangue materials are separated from the impure Na_2WO_4 solution by filtration (Lassner and Schubert, 1999).

3.3.2. Silica and molybdenum precipitations

The purer Na_2WO_4 solution from the filtration still contains various impurities, such as silica and molybdenum (Wolfe et al., 2014). In the silica precipitation process, silica and some other impurities are removed by the addition of 0.1 kg aluminum sulfate solution ($Al_2(SO_4)_3 \cdot 18H_2O$) and 0.04 kg magnesium sulfate solution ($MgSO_4 \cdot 7H_2O$) per kg tungsten (Lassner and Schubert, 1999). The precipitates, e.g. $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$ and $2MgO \cdot SiO_2$, become solid waste.

Typical high-grade scheelite and wolframite concentrates furthermore contain 0–2% and 0–0.003% molybdenum as sodium molybdate (Na_2MoO_4), respectively (Lassner and Schubert, 1999; Yih and Wang, 1979). In the molybdenum precipitation process, the molybdenum is removed to negligible levels (<100 ppm) (Upadhyaya, 1998) by the addition of sodium hydrosulfide (NaHS) in 2–2.5 times the stoichiometric requirement of R3 (Wolfe et al., 2014). An excess of NaHS is required since it is also consumed by other impurities. Sulfuric acid (H_2SO_4) is required in the molybdenum precipitation itself (R3) but also in order to neutralize the NaOH that is formed during R3 as well as to neutralize excess Na_2CO_3 and NaOH added in the sodium carbonate and hydroxide digestion processes (R4 and R5) (Wolfe et al., 2014):

$$4NaHS + Na_2MoO_4 + H_2SO_4 \rightarrow MoS_3 + H_2S + Na_2SO_4 + 4NaOH \quad (R3)$$

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + H_2O \quad (R4)$$

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2 \quad (R5)$$
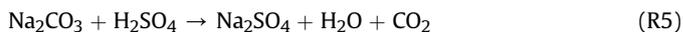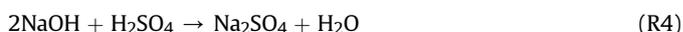
Note that excess Na_2CO_3 is only present in the scheelite route, while excess NaOH is only present in the wolframite route. This excess is of varying magnitude and can even be zero if removed during the previous silica precipitation. The BC, LC and HC all include the amount of H_2SO_4 needed for R3 and to neutralize the NaOH formed during R3. In addition, it is assumed that all the excess Na_2CO_3 and NaOH need to be neutralized in the HC, while half of the excess need to be neutralized in the BC and none in the LC (assuming then complete removal during silica precipitation). The amount of added H_2SO_4 was calculated based on the stoichiometry of the chemical reactions R3, R4 and R5 with the assumption of a 95% stoichiometric efficiency (Hischier et al., 2005).

The molybdenum trisulfide (MoS_3) precipitate is removed by filtration and the resulting filtration cake is washed with four times 2.3 kg H_2O per kg solid filtration cake (Yih and Wang, 1979). The H_2O applied for washing of the filtration cake becomes liquid aqueous waste after use. In the case of scheelite, emissions of CO_2 originating from the Na_2CO_3 input are formed during the silica and molybdenum precipitations (Lassner and Schubert, 1999), and were calculated based on a molar ratio of 1:1 between CO_2 and Na_2CO_3.

The MoS_3 precipitate becomes solid waste, while the hydrogen sulfide (H_2S) and CO_2 formed in R3 and R5, respectively, were assumed to be emitted to air (Wolfe et al., 2014).

3.3.3. Solvent extraction

Tungsten is here extracted from the purified Na_2WO_4 solution by an organic solvent mixed with H_2SO_4. The extract is washed with deionized H_2O and then the organic solvent is stripped from tungsten by the addition of NH_3 (Wolfe et al., 2014), resulting in an ammonia tungstate (($NH_4)_2WO_4$) solution. Typical inputs are 40 kg organic solvent (7.3% alamine 336, 7.4% decanol and 85% kerosene), 3.2 kg 5% H_2SO_4 solution, 8.5 kg deionized H_2O and 12 kg 5% NH_3 solution per kg tungsten (Yih and Wang, 1979). The Na_2SO_4 formed during solvent extraction and from $Al_2(SO_4)_3$, $MgSO_4$ and H_2SO_4 in previous processes becomes liquid aqueous waste together with the deionized wash H_2O in this step. The amount of separated Na_2SO_4 was calculated based on a molar ratio of 3, 1 and 1 to the inputs of $Al_2(SO_4)_3$, $MgSO_4$ and H_2SO_4, respectively. The stripped organic solvent becomes recovered to an unknown degree (Lassner and Schubert, 1999), why 95% was assumed based on Geisler et al. (2004). A fugitive loss of 2% emitted to air was assumed for the NH_3 (Jiménez-González et al., 2000) and the required input was calculated acknowledging that NH_3 is partly recovered in the later crystallization and calcination processes (Section 3.3.4 and 3.4.1) and led back to the solvent extraction.

3.3.4. Crystallization

In the crystallization process, the ($NH_4)_2WO_4$ solution is treated so that NH_3 and H_2O vaporizes and APT (($NH_4)_{10}(H_2W_{12}O_{42})\cdot4H_2O$) is formed (Wolfe et al., 2014). The NH_3 evaporated in the crystallization process is 58% of the NH_3 input (minus the fugitive loss) to the solvent extraction process based on the differing NH_3 content of ($NH_4)_2WO_4$ and APT (Wolfe et al., 2014). This NH_3 can be recovered to the solvent extraction process after condensation. The other 42% NH_3 evaporates in the later calcination process (Lassner and Schubert, 1999). A NH_3 recovery of 23–99% was applied based on Ashtari et al. (2016). The APT formed is first filtered, washed with deionized H_2O and then dried (Lassner and Schubert, 1999). The deionized H_2O used for washing as well as the filtered liquid are effectively recovered completely (Lassner and Schubert, 1999).

3.4. Pyrometallurgy

The energy needed in pyrometallurgy to produce WC powder from APT is 3.5–12 kWh/kg WC (EC, 2001).

3.4.1. Calcination

The calcination process is predominantly carried out in rotary furnaces at temperatures of 400–900 °C (Naboychenko et al., 2009), where advantage is taken of the reducing capacity of the gases formed during decomposition of APT into tungsten blue oxide (TBO), gaseous NH_3 and H_2O (Lassner and Schubert, 1999). TBO is a combination of WO_3, $W_{20}O_{58}$ (corresponding to $WO_{2.9}$) and $W_{18}O_{47}$ (corresponding to $WO_{2.6}$), but for the calculations in this study it was assumed to be only WO_3. The NH_3 recovery was set to 23–99% as in Section 3.3.4 and led back to the solvent extraction process.

3.4.2. Hydrogen reduction

Hydrogen (H_2) reduction converts TBO to tungsten metal powder and is typically conducted in push-type furnaces with a 2.5–40 stoichiometric H_2 excess (Lassner and Schubert, 1999; Wolfe et al., 2014). A fugitive loss of 0.5% H_2 emitted to air was assumed based on Jiménez-González et al. (2000). Dopants (e.g. salts of alkali metals) are added to the TBO in 50–500 ppm amounts to affect the

grain size (Wolfe et al., 2014), but these small amounts were disregarded. Excess H_2 is effectively recovered completely in hydrogen regeneration systems (Naboychenko et al., 2009).

3.4.3. Carburization

Carburization is commonly conducted by introducing tungsten metal powder blended with carbon black (Lassner and Schubert, 1999) in a furnace with a reducing H_2 atmosphere at temperatures of 1200–2000 °C (Wolfe et al., 2014). The calculations were based on the following chemical reactions (Lassner and Schubert, 1999):

$$W + C \rightarrow WC \tag{R6}$$

$$C + 2H_2 \rightarrow CH_4 \tag{R7}$$

$$2C + H_2 \rightarrow C_2H_2 \tag{R8}$$

In the WC powder, the carbon content is 6.1% and an additional 2–10% excess is typically used in R6 (Yih and Wang, 1979). The H_2 input reacts into either methane (CH_4) when the temperature is ≤ 1600 °C (R7) or acetylene (C_2H_2) when the temperature is > 1600 °C (R8) (Lassner and Schubert, 1999). This enhances the diffusion of carbon into the tungsten metal powder (Lassner and Schubert, 1999). Due to limited data, it was assumed that the input of H_2 is added as in R7 and R8 with a 95% stoichiometric efficiency (Hischier et al., 2005) and a 0.5% fugitive loss of H_2 emitted to air was assumed based on Jiménez-González et al. (2000). In the LC, R8 was used for the calculations of the amount H_2 needed due to lower input, while R7 was used in the HC. In the BC, half of the carbon reacts according to R7 and the other half according to R8. The H_2 going out from the carburization process is burned off at the end of the furnace (Yih and Wang, 1979), and the same was assumed for excess CH_4 and C_2H_2, thus leading to CO_2 emissions to air.

3.5. Powder metallurgy

An estimate for the energy requirement in powder metallurgical manufacturing in general of 2–20 kWh/kg sintered product was obtained from Kruzhanov and Arnhold (2012) and was assumed to represent production of sintered WC-Co from WC powder, specifically.

3.5.1. Powder milling

WC powder is here mixed together with cobalt powder, a solvent and additives. This mixture is then milled in order to obtain the desired particle size (Mehrotra, 2014). The share of WC plus cobalt powder in the mixture was set at 50% based on general spray drying of metal powders (Fauchais et al., 2014), and the cobalt content of this share is 6–16% (Section 2.1). Conventionally in powder milling of cemented carbides, hydrocarbon solvents are used (Soares et al., 2011) and C_7H_{16} as well as C_6H_{14} are the most common (Lassner and Schubert, 1999). In addition, paraffin wax is commonly used as additive at a 1–3% share of the mixture (Lassner and Schubert, 1999). Which solvent and amounts to be used in the BC, LC and HC was determined based on the respective CED of C_7H_{16}, C_6H_{14} and paraffin wax (Ecoinvent database, 2017) to ensure that the HC results in highest environmental impacts and *vice versa* (Table 3). Based on their respective boiling temperatures, a fugitive loss of 1% was applied for C_7H_{16} and C_6H_{14} (Jiménez-González et al., 2000). The net input of organic solvent is furthermore affected by the degree of recovery in the later granulation and compaction process (Section 3.5.2).

3.5.2. Granulation and compaction with subsequent sintering

Granulation is typically carried out via spray drying at 100–130 °C, which causes the solvent from the powder milling to evaporate and spherical powder granules to take form (Lassner and Schubert, 1999). Nitrogen gas (N_2) is typically used (Mehrotra, 2014) and the required input in kg/kg of dried powder (m_{N_2}) was calculated, by assuming a cylindrical chamber, as:

$$m_{N_2} = \rho_{N_2} \times \left(f \times \pi \times (d/2)^2 \right) \Big/ c \tag{1}$$

where ρ_{N_2} is the density of N_2 [kg/m^3], f is the flow rate of N_2 [m/s], d is the diameter of the chamber and c is the capacity of spray drying [kg dried powder/s]. In spray drying of non-ferrous metal powders in general, the maximum air rate is typically 0.3–0.5 m/s per the total cross-section of the chamber (Neikov, 2009) and this was used as an estimate of the N_2 flow rate. The capacity of a typical spray drier for WC-Co production is 120–180 kg/h with a diameter of 2 m (Lassner and Schubert, 1999). A fugitive loss of 0.5% N_2 emitted to air was assumed (Jiménez-González et al., 2000). The solvent from the previous powder milling process and the N_2 gas can both be recovered (Mehrotra, 2014). A 95% recovery of the organic solvent was assumed based on Geisler et al. (2004) and nitrogen was set to be recovered completely through condensation (Mehrotra, 2014). Unrecovered amounts of C_7H_{16} and C_6H_{14} were assumed to be emissions to air. About 5% of the powder remains un-granulated and is typically recycled into the powder milling process or scrapped (Lassner and Schubert, 1999; Mehrotra, 2014). Therefore, the yield of WC and cobalt powder, also containing paraffin, is 95–100%. After granulation, the powder granules are typically compacted to the desired product shape (Lassner and Schubert, 1999). Vacuum sintering is then conducted to obtain the final cemented WC-Co product (German, 2014). In this process, the cobalt powder forms a cement for the WC powder. The paraffin wax is removed as vapor (Mehrotra, 2014) and was assumed to be emitted to air.

3.6. Recycling

Several methods for recycling of tungsten have been developed in response to the large variety of tungsten scrap available (Shemi et al., 2018). Chemical and zinc recycling are the two main recycling processes for tungsten, covering about 50% of the total tungsten recycling each (Leal-Ayala et al., 2015).

3.6.1. Chemical recycling

Chemical recycling methods imply recycling that is conducted via the hydrometallurgy route to obtain APT (Leal-Ayala et al., 2015) and typically involve oxidation of tungsten scrap by electrical energy, chemicals or air in order to make the scrap soluble in alkaline solutions (Lassner and Schubert, 1999). In response to limited data availability, this study assumes chemical recycling by electrolytic dissolution, where scrap with a 40–95% tungsten content acts as the anode of a NaOH electrolyte in which the scrap becomes oxidized and digested (Lassner and Schubert, 1999). The energy

Table 3
Calculated shares of heptane (C_7H_{16}), hexane (C_6H_{14}) and paraffin wax in the powder milling mixture. BC = baseline case, LC = low environmental impact case and HC = high environmental impact case.

Material	BC	LC	HC
C_7H_{16}	24%	0%	47%
C_6H_{14}	24%	49%	0%
Paraffin wax	2%	1%	3%

requirement is 2–11 kWh/kg processed tungsten depending on the scrap type (Hairunnisha et al., 2007; Lassner and Schubert, 1999). Input of 0.96 kg NaOH/kg tungsten is required and the yield is 90–100% tungsten (Hairunnisha et al., 2007). Excess NaOH was calculated based on that 1 mol of tungsten requires 2 mol of NaOH. All excess NaOH remaining after the silica precipitation again need to be neutralized by H_2SO_4 in the molybdenum precipitation as described in Section 3.3.2 (all excess neutralized in the HC, half of the excess neutralized in the BC and no excess assumed in the LC). The impure Na_2WO_4 solution out from the chemical recycling process also contains insoluble metal oxides, such as cobalt and tantalum, which are separated in the filtration process (Lassner and Schubert, 1999). Recovery of these metal oxides is typically not conducted, not even for the most abundant metal cobalt (Shibata et al., 2014). Thus, the metal oxides were assumed to be solid waste. After the chemical recycling process, the impure Na_2WO_4 solution enters the virgin production route at the filtration of the hydrometallurgy phase (Fig. 1).

3.6.2. Zinc recycling

In zinc recycling, the scrap must have the same composition and similar purity as the final product (Lassner and Schubert, 1999). The cobalt binder in the WC-Co scrap becomes alloyed with molten zinc (Freemantle and Sacks, 2015; Wolfe et al., 2015). The zinc is then distilled off and collected for recovery, while the remaining porous cake is crushed, milled and the resulting powder is used together with virgin WC and cobalt powder in the powder milling process (Wolfe et al., 2015). The energy requirement is 1.5–4 kWh/kg of WC and cobalt powder output (Acharyulu and Rama Rao, 1996; EC, 2001). A fugitive loss of zinc at 0.5% during distillation was assumed to be emitted to air based on Jiménez-González et al. (2000), while the remaining zinc is effectively recovered completely (Wolfe et al., 2015). The yield in the zinc recycling process is 97–98% WC-Co and 1–1.3 kg zinc/kg WC-Co is required (Upadhyaya, 1998). The WC-Co lost become solid waste.

4. Results and discussion

4.1. Life cycle inventory data

Comprehensive and ready-to-use LCI data for the typical non-Chinese production of 1 kg WC-Co is shown in Table 4. The LCI data results for the other scenarios, varying the recycling rate and the type of tungsten ore, are shown in Section S4 in the SM and all the unit process data results are presented in Section S3 in the SM. As can be seen in Table 4, the production of WC-Co requires many different inputs. Regarding energy input, the largest inputs of diesel and electricity per kg WC-Co are in the mining and powder metallurgy phases, respectively. The largest material inputs per kg WC-Co are kerosene, deionized H_2O, Na_2CO_3 and H_2O, which are all added in ≥1 kg/kg WC-Co each.

A comparison was made between the LCI from this study and that from Syrrakou et al. (2005) for the production of 1 kg of WO_3 (Table 5). Inputs from this study are generally in the same order of magnitude as the inputs by Syrrakou et al. (2005). Exceptions are the input of sodium hydroxide and sulfuric acid, which are notably lower in this study. The latter can possibly be due to assumptions regarding neutralization requirements for the sulfuric acid. Note that a large number of additional inputs and outputs that were quantified in this study are not shown in Table 5 since they were not provided by Syrrakou et al. (2005).

A comparison was also made with LCI results for the production of 1 kg WC powder in China provided by Ma et al. (2017), focusing here on energy requirement since most other inputs are qualitatively different between the productions (Table S18, SM) and can

Table 4
Life cycle inventory data for the typical non-Chinese production of tungsten carbide with cobalt (WC-Co). All values are in kg/functional unit (f.u) unless otherwise noted. The functional unit is 1 kg WC-Co with a cobalt content of 6–16% and a WC grain size >0.2 μm. BC = baseline case, LC = low environmental impact case and HC = high environmental impact case.

Input or output	Parameter	BC	LC	HC	Comment
MINING					
Input	Anyl xanthate	0.0028	0.0024	0.0031	
Input	Diesel	16	6.4	35	MJ/f.u
Input	Electricity	1.6	2.1	0	kWh/f.u
Input	Frother	0.0029	0.0012	0.0048	
Input	Oleic acid	0.036	0.019	0.054	
Input	Pine oil	0.00055	0.00048	0.00062	
Input	Scheelite ore	140	91	230	
Input	Sodium carbonate	0.18	0.023	0.35	
Input	Sodium cyanide	0.014	0.0024	0.027	
Input	Sodium silicate	0.12	0.048	0.20	
Input	Sodium sulfide	0.069	0.061	0.078	
Input	Tannin	0.020	0.0024	0.040	
Input	Water	150	100	230	
Input	Wolframite ore	48	31	78	
Output	Carbon dioxide	0.10	0.055	0.15	Emitted to air
Output	Separated material	190	120	310	Tailings, landfilled. Base case: Half non-sulfidic and half sulfidic. LS: non-sulfidic. HS: sulfidic
Output	Separated flotation reagents	0.41	0.14	0.70	Landfilled with tailings
TRANSPORT					
Input	Transport by lorry	6.1	5.7	6.8	ton·km/f.u
HYDROMETALLURGY					
Input	Alamine 336	0.11	0.10	0.12	
Input	Aluminum sulfate	0.040	0.037	0.042	
Input	Ammonia	0.19	0.013	0.39	
Input	Decanol	0.11	0.10	0.12	
Input	Deionized wash water	6.5	6.1	6.9	
Input	Electricity	2.0	1.2	3.2	kWh/f.u
Input	Kerosene	1.3	1.2	1.4	
Input	Magnesium sulfate	0.014	0.013	0.015	
Input	Sodium carbonate	1.0	0.68	1.3	
Input	Sodium hydrosulfide	0.051	0	0.13	
Input	Sodium hydroxide	0.13	0.11	0.16	
Input	Sulfuric acid	0.54	0.12	1.3	
Input	Tungsten scrap	0.14	0.079	0.32	
Input	Water	18	17	19	
Output	Alamine 336	0.11	0.10	0.12	Liquid organic waste
Output	Ammonia gas	0.12	0.012	0.23	Emitted to air
Output	Carbon dioxide	0.30	0.17	0.43	Emitted to air
Output	Decanol	0.11	0.10	0.12	Liquid organic waste
Output	Deionized wash water	6.5	6.1	6.9	Liquid aqueous waste
Output	Gangue	0.96	0.76	1.2	Solid waste
Output	Hydrogen sulfide	0.0035	0	0.0081	Emitted to air
Output	Kerosene	1.3	1.2	1.4	Liquid organic waste
Output	Molybdenum sulfide	0.020	0	0.046	Solid waste
Output	Sodium sulfate	0.84	0.23	1.9	Liquid aqueous waste
Output	Wash water	0.18	0	0.43	Liquid aqueous waste
PYROMETALLURGY					
Input	Carbon black	0.053	0.048	0.058	
Input	Electricity	6.3	2.7	10	kWh/f.u
Input	Hydrogen	0.039	0.028	0.052	
Output	Ammonia gas	0.076	0.0018	0.16	Emitted to air
Output	Carbon dioxide	0.011	0.0034	0.019	Emitted to air
Output	Hydrogen	0.0027	0.00031	0.0054	Emitted to air
POWDER METALLURGY					
Input	Cobalt powder	0.10	0.15	0.055	
Input	Electricity	11	2.1	21	kWh/f.u
Input	Nitrogen	0.13	0.073	0.21	
Input	Organic solvent	0.059	0.059	0.059	
Input	Paraffin wax	0.041	0.020	0.063	
Input	WC-Co scrap	0.12	0.10	0.14	
Input	Zinc	0.00067	0.00048	0.00094	
Output	Nitrogen	0.13	0.073	0.21	Emitted to air
Output	Organic solvent	0.059	0.059	0.059	Emitted to air
Output	Paraffin	0.040	0.020	0.060	Emitted to air
Output	Sintered WC-Co	1.0	1.0	1.0	f.u
Output	Un-granulated powder	0.027	0	0.056	Solid waste
Output	WC-Co loss	0.0029	0.0019	0.0043	Solid waste
Output	Zinc	0.00067	0.00048	0.00094	Emitted to air

Table 5

Comparison between inputs for the baseline case for typical non-Chinese production of 1 kg of tungsten trioxide (WO_3) in this study and from Syrrakou et al. (2005). Note that the comparison is only made with the data provided by Syrrakou et al. (2005) and that ammonium hydroxide (ammonia dissolved in water) was not included in this comparison since ammonia and water inputs were reported separately in this study.

Input [kg/kg WO_3]	WO_3 production, this study	WO_3 production, Syrrakou et al. (2005)
Aluminum sulfate solution	0.08	0.08
Magnesium sulfate solution	0.03	0.03
Sodium carbonate or soda ash	1.23	1.37
Sodium hydroxide	0.14	1.03
Sodium sulfide	0.07	0.05
Sulfuric acid	0.56	1.4

only be compared on LCIA level. A comparison between LCIA results for Chinese WC production and the typical non-Chinese WC production from this study is therefore provided in Section 4.2. The baseline case for the typical non-Chinese production scenario in this study results in 11 kWh electricity and 17 MJ diesel (corresponding to 58 MJ-eq), compared with 47 kWh electricity (170 MJ-eq) in the study by Ma et al. (2017). This suggests that the non-

Chinese production is more energy efficient and is in line with the by Ma et al. (2017) stated immaturity of the Chinese tungsten industry compared to advanced world levels. The energy requirement in the Chinese WC production is dominated by the mining of tungsten ore and production of tungsten concentrates (110 MJ-eq) and tungsten carbide production (56 MJ-eq) (Ma et al., 2017). In the non-Chinese WC production, energy requirement is dominated by mining (24 MJ-eq) and pyrometallurgy (25 MJ-eq). Thus, Chinese and non-Chinese WC production show similar hotspots regarding energy requirement.

4.2. Life cycle impact assessment and scenario analysis

LCIA results per 1 kg WC-Co for CED (total), climate change, terrestrial acidification, freshwater eutrophication, water depletion and landfilling are shown in Fig. 2. In general, it is the mining, hydrometallurgy and powder metallurgy phases that contribute the most to the impact categories. It is also clear from Fig. 2 that a high recycling reduces all impacts notably, in particular freshwater eutrophication and landfilling.

Fig. 2a shows that the hydrometallurgy and powder metallurgy phases generally contribute the most to the total CED. The inputs of kerosene (10−32% of the total CED) in the hydrometallurgy phase
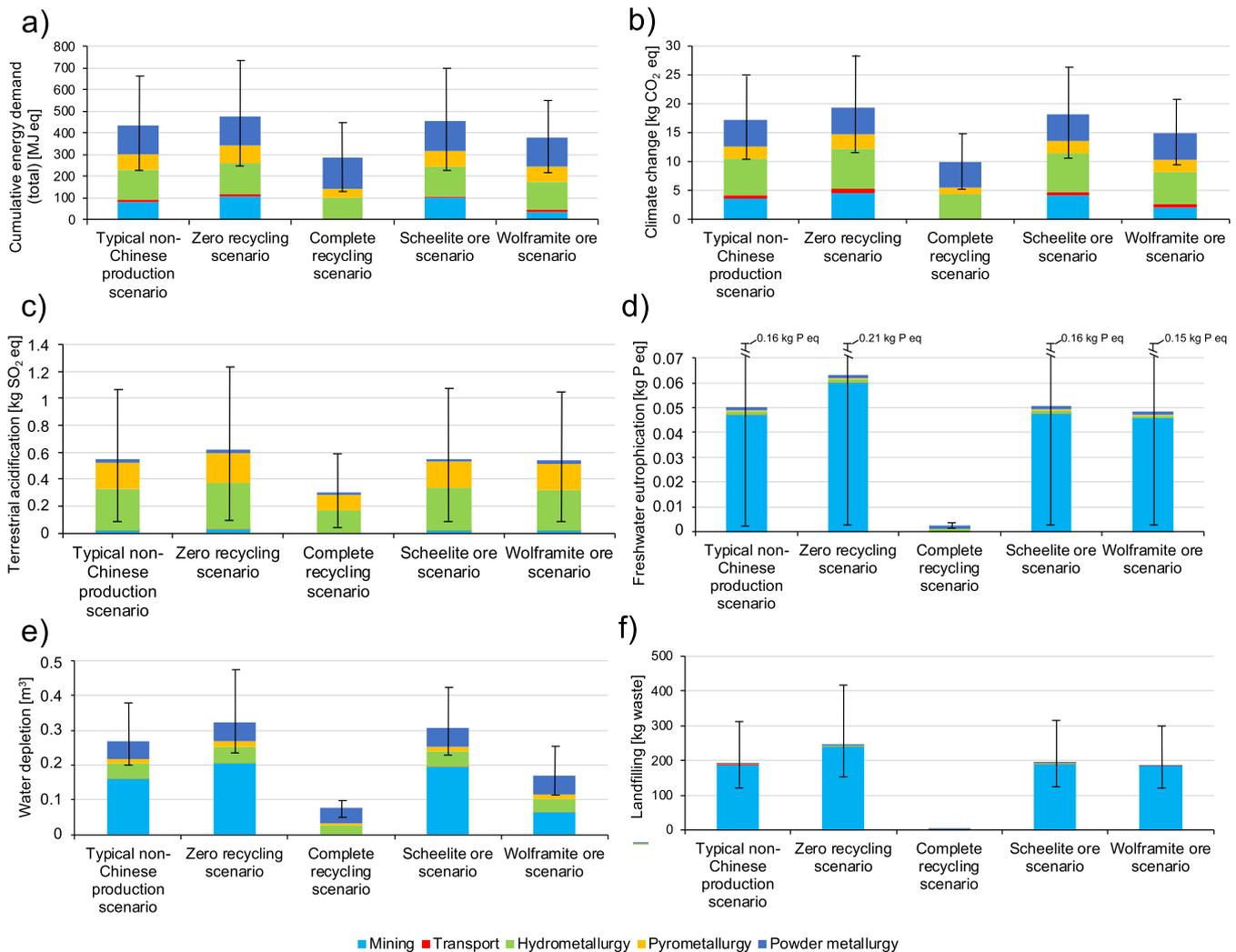
Fig. 2. LCIA results per kg tungsten carbide with cobalt (WC-Co) for different scenarios. a) Cumulative energy demand (total). b) Climate change. c) Terrestrial acidification. d) Freshwater eutrophication. e) Water depletion. f) Landfilling. Bars show the baseline case and ranges the low and high environmental impact cases.

as well as the electricity required (8–51%) in the powder metal-lurgy phase have the largest contribution to the total CED. Mining, mainly due to inputs of diesel and tannin, and pyrometallurgy due to electricity required, also contributes notably in several of the scenarios. The hydrometallurgy and powder metallurgy phases generally also contribute the most to climate change (Fig. 2b). The largest contribution to climate change comes from treatment of the kerosene output from hydrometallurgy as liquid organic waste (10–25%) and electricity required in powder metallurgy (5–45%). Fig. 2c shows that the hydrometallurgy and pyrometallurgy phases contribute the most to terrestrial acidification. The largest contri-butions are from emissions of NH_3 in hydrometallurgy and pyro-metallurgy with 33–54% and 5–37% to terrestrial acidification, respectively.

In the cases of freshwater eutrophication, water depletion and landfilling, the mining phase generally has the largest contribution. For freshwater eutrophication, the largest contribution comes from separated gangue in mining in the BC and HS, mainly due to the emission of nutrients from the treatment of sulfidic tailings (93–97%). In the LC, the freshwater eutrophication is considerably lower since all separated gangue was assumed to be non-sulfidic. Thus, whether tailings are sulfidic or not greatly influences the results for freshwater eutrophication. Furthermore, considering the toxic elements (e.g. arsenic and iron) that might leach out from these tailings (Liu et al., 2010; Pé-Leve Santos et al., 2014), we speculate that these might also have impacts on human health and on the environment.

The input of H_2O for the gravity methods and the sulfide flota-tion during mining have the largest contribution to water depletion in the typical non-Chinese production, zero recycling and scheelite ore scenarios (53–68%). In the complete recycling scenario, where all tungsten input come from scrap and no mining thus occurs, the production of cobalt (8–44% of the total water depletion) and electricity required (11–45%) in the powder metallurgy phase have the largest contribution. In the wolframite ore scenario, the H_2O input for the gravity methods generally has the largest contribution to water depletion.

The separated material in the mining phase clearly has the largest contribution to landfilling (>98%) for all scenarios except in the complete recycling scenario where there is no mining phase since all tungsten input comes from scrap. In that scenario, most of the comparatively minor landfilling instead occurs during the hy-drometallurgy phase in the form of separated gangue.

The LCIA results for photochemical oxidant formation, ozone depletion, and CED (fossil and renewable) are shown in Section S5 in the SM. In the case of photochemical oxidant formation, emis-sions of organic solvent and paraffin in powder metallurgy have the largest contributions with 26–61% and 15–40%, respectively. The largest contribution to ozone depletion is caused by the inputs of kerosene to hydrometallurgy (15–43%) and the electricity required in powder metallurgy (6–43%). Inputs of kerosene in the hydro-metallurgy phase (17–39% of the fossil CED) and electricity required in the powder metallurgy phase (5–41%) constitute the largest contributions to the fossil CED. In the case of renewable CED, inputs of tannin in mining (10–50% of the renewable CED) and electricity needed in powder metallurgy (10–30%) have the largest contribution in all scenarios except in the complete recycling and wolframite ore scenarios where there is no input of tannin. In the complete recycling and wolframite ore scenarios, the largest con-tributions to the renewable CED are in general from electricity required in pyrometallurgy and powder metallurgy with 16–28% and 14–61%, respectively.

The included impact categories in this study were chosen following Santero and Hendry (2016) and the LCIA was conducted in order to illustrate the applicability of the LCI data as well as to identify environmental hotspots. However, other impact categories, such as for example human toxicity and ecotoxicity, could still be interesting to consider in future studies as well. Another example is abiotic resource use impacts, which might be included once established methods for such impact assessment are in place (Santero and Hendry, 2016).

A comparison between the LCIA results for the typical non-Chinese WC production in this study and Chinese WC production (Ma et al., 2017) was also conducted. Table 6 shows that the LCIA results for the typical non-Chinese WC production are lower for climate change, photochemical oxidant formation and water depletion, but higher for terrestrial acidification, ozone depletion and freshwater eutrophication. The largest contributions to climate change in Chinese WC production were emissions of greenhouse gases, such as CO_2, from coal-based electricity generation in both tungsten ore mining and concentration and in the process of WC production from APT. In non-Chinese WC production on the other hand, the treatment of kerosene output from hydrometallurgy as liquid organic waste, input of diesel in mining as well as electricity in pyrometallurgy contribute the most to climate change. In Chi-nese WC production in the case of photochemical oxidant forma-tion, emissions of nitrogen oxides (NO_x) from coal-based electricity generation in tungsten ore mining and concentration as well as in WC production from APT dominated the contribution. In non-Chinese WC production, the input of diesel in mining had the largest influence on photochemical oxidant formation. In contrast to this study, where direct emissions of ammonia in hydrometal-lurgy and pyrometallurgy dominate the contribution to terrestrial acidification, the main contribution to this impact category in the study by Ma et al. (2017) were in turn emissions of SO_2 and NO_x from coal-based electricity production in tungsten ore mining and concentration. Notably, no direct emissions from the foreground system are indicated in the LCI data provided by Ma et al. (2017). A contribution analysis to the impact categories of ozone depletion, water depletion and freshwater eutrophication are not provided by Ma et al. (2017), rendering a detailed comparison with the typical non-Chinese WC production difficult.

There are a number of uncertainties in this study, as illustrated by Fig. 2, where the scenarios reflect model uncertainties and the bars imply parameter uncertainties, see further Section 4.3. The scenarios constructed besides the typical non-Chinese production scenario probably do not represent realistic scenarios. For example, complete recycling would be difficult to achieve due to technical limitations and since materials deteriorate during use. However, differences between scenarios using the current recycling rate and the scenario with complete recycling show that recycling greatly reduces environmental impacts. There is also a weaker indication

Table 6
Comparison of life cycle impact assessment results for the baseline case for typical non-Chinese production in this study and Chinese production in the study by Ma et al. (2017) of 1 kg of tungsten carbide (WC) powder. Note that the impact cate-gories of cumulative energy demand (CED) (total, fossil and renewable) and land-filling are not presented as they were not available from Ma et al. (2017).

Impact category	Chinese WC production (Ma et al., 2017)	Typical non-Chinese WC production (baseline case, this study)
Climate change [kg CO_2 eq]	69	14
Photochemical oxidant formation [kg NMVOC eq]	0.18	0.049
Terrestrial acidification [kg SO_2 eq]	0.21	0.58
Ozone depletion [kg CFC-11 eq]	$4.8 \cdot 10^{-7}$	$2.6 \cdot 10^{-6}$
Water depletion [m³]	0.60	0.24
Freshwater eutrophication [kg P eq]	0.00028	0.054

that the use of wolframite ore instead of scheelite ore as a source of tungsten implies less environmental impacts. Further analysis is recommended in order to compare other processes for recycling, especially for chemical recycling, since this process typically differs a lot due to the many types of tungsten scrap available (Shemi et al., 2018).

4.3. Sensitivity analysis

The results from the sensitivity analysis of parameters for which ranges were available are provided in Table 7. Only parameters causing changes larger than ±10% relative the BC for at least one of the included impact categories are shown. The results show that in particular five parameters contribute substantially to the uncertainty. The tungsten content in workable ores as well as tungsten yield in gravity methods and grinding process of scheelite ore are critical for the impacts of freshwater eutrophication and landfilling. This can be explained by the fact that a lower tungsten content and lower tungsten yield implies an increased amount of gangue material, which is landfilled. The recovery of NH_3 as well as the paraffin share of the powder milling mixture clearly have a strong influence on the impacts of terrestrial acidification and photochemical oxidant formation, respectively. This is because unrecovered NH_3 and the paraffin removed during sintering both become direct emissions. The data on energy requirement during powder metallurgy was here based on general powder metallurgical manufacturing, which is reflected in the wide range for this parameter and explains why it was identified as critical in the sensitivity analysis. More detailed information on the energy requirement in powder metallurgy of WC-Co, specifically, would reduce this uncertainty.

Results from the sensitivity analysis of parameters for which no ranges were available indicated that eight such parameters caused changes larger than ±10% relative the BC for at least one of the included impact categories. These parameters are (1) the share of scheelite in the low tungsten concentration fraction, (2) the share of the scheelite output that is in the high concentration fraction, (3) the input of organic solvent to solvent extraction, (4) the share of this input that is kerosene, (5) the input of NH_3 to the solvent extraction, (6) the recovery of organic solvent applied in solvent extraction, (7) the share of WC and cobalt powder in the powder milling mixture as well as (8) the recovery of organic solvent in the processes of granulation and compaction with subsequent sintering. Although it is unsure whether ±50% is a reasonable range for these parameters, this analysis illustrates, for example, the importance of effective organic solvent recovery, since a lowering of these recovery rates notably increases impacts. These parameters should be subject to further investigation and effort is needed to obtain more realistic ranges for them.

5. Conclusions

This study provides ready-to-use cradle-to-gate LCI data and LCIA results for the typical non-Chinese production of WC-Co. LCI data is furthermore provided for a number of WC-Co precursors: APT, TBO, tungsten metal and WC powder. This LCI data can be readily used in generic LCA studies involving WC-Co or one of its precursors as input. For more specific studies where the exact origin of the WC-Co is known, alterations in the LCI data may be required to adequately represent that particular WC-Co or precursor production. The LCI results in this study are of similar magnitude or lower compared to previous studies of the production of WC-Co precursors outside China. The results also indicate that the typical non-Chinese production is less energy-intensive than the Chinese production.

The LCIA results show that the mining, hydrometallurgy and powder metallurgy phases generally dominate the cradle-to-gate life cycle impacts and that only a limited number of inputs and outputs are responsible for a large share of the total contribution to the included impact categories. The largest contribution to the total CED in general comes from inputs of kerosene in the hydrometallurgy phase as well as the electricity required in the powder metallurgy phase. Treatment of the kerosene output from hydrometallurgy as liquid organic waste and electricity required in powder metallurgy have the largest contribution to climate change. In the case of terrestrial acidification, the largest contributions are from emissions of NH_3 in the hydrometallurgy and pyrometallurgy phases. Emissions of nutrients from the treatment of sulfidic tailings in general have the largest contribution to freshwater eutrophication. The largest contribution to water depletion in general comes from the input of H_2O for the gravity methods and the sulfide flotation during mining. In the case of landfilling, the separated material in the mining phase generally has the largest contribution. Emissions of organic solvent and paraffin in powder metallurgy have the largest contributions to photochemical oxidant formation. The largest contribution to ozone depletion is caused by the inputs of kerosene to hydrometallurgy and the electricity required in powder metallurgy. Inputs of kerosene in the hydrometallurgy phase and electricity required in the powder metallurgy phase constitute the largest contributions to the fossil CED. In the case of renewable CED, inputs of tannin in mining and electricity needed in powder metallurgy in general have the largest contribution to the renewable CED. Recycling was shown to greatly reduce the impacts, with reductions of 22—100% for the complete recycling compared to the typical production scenario. Additional assessments of various recycling processes are recommended for future studies. Furthermore, the sensitivity analysis indicated that future data improvements for a limited number of parameters potentially could reduce uncertainties significantly.

Table 7
Sensitivity analysis of parameters for which ranges were available. Results show relative changes versus the baseline case (BC) for the typical non-Chinese tungsten carbide with cobalt (WC-Co) production scenario. Only parameters causing a change larger than ±10% relative the BC are shown. LC = low environmental impact case, HC = high environmental impact case, NH_3 = ammonia, WC = tungsten carbide, CC = climate change, TA = terrestrial acidification, FE = freshwater eutrophication, POF = photochemical oxidant formation, OD = ozone depletion, CED (total) = total cumulative energy demand, LF = landfilling.

Parameter	LC	HC
Tungsten content in workable ores (gravity methods and grinding process)	−16% FE	+23% FE
	− 17% LF	+25% LF
Tungsten yield, scheelite ore (gravity methods and grinding process)	−10% FE	+12% FE
	−10% LF	+13% LF
Recovery of NH_3 (crystallization and calcination processes)	−80% TA	+80% TA
Energy requirement, production of WC-Co from WC (powder metallurgy)	−16% CC	+16% CC
	−18% OD	+18% OD
	−21% CED (total)	+21% CED (total)
Paraffin share of the mixture (powder milling)	−12% POF	+12% POF

A comparison of non-Chinese and Chinese WC production showed that LCIA results in non-Chinese WC production were lower for climate change, photochemical oxidant formation and water depletion, but higher for terrestrial acidification, ozone depletion and freshwater eutrophication. The main contributors to these impact categories were in general coal-based electricity generation in Chinese WC production while various inputs and outputs, e.g. input of diesel to mining and direct emissions of ammonia in the hydrometallurgy and pyrometallurgy phases, contributed the most to the impact categories in non-Chinese WC production.

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Appendix A. Supplementary material

Supplementary material to this article can be found online at https://doi.org/10.1016/j.jclepro.2018.10.272.

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