Abschlussbericht zum Teilvorhaben „Prozess-und Systemsimulation für eine nachhaltige Legierungsentwicklung und –herstellung“ im Verbundprojekt: „Datenökosystem für die digitale Materialentwicklung auf Basis Ontologie-basierter digitaler Repräsentationen von Kupfer und Kupferlegierungen“

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Teil 1: Kurzbericht (wird veröffentlicht)

The work packages assign to HZDR have focused on the recycling of copper. The present study consists of ontology development of copper recycling processes aiming to the production of copper alloys. Accordingly, corresponding process models have been developed followed by environmental impacts assessment. The key challenge of the aforementioned steps is that copper recycling is complexly intertwined with recycling of other materials. The most copper containing waste streams also contain various other elements and many processing steps have multiple different inputs and outputs including copper and non-copper streams, which all have their own environmental impacts that need to be considered to provide a fair assessment of copper recycling and production. The current study employed HSC Chemistry and FactSage software to model and simulate copper alloy process from copper scrap (CuScrap) and waste printed circuit boards (WPCBs). Results were represented in tables and sematic graphs for various processes and materials occurring in a complex network. Three simulation cases based on different compositions of CuScrap and WPCBs were examined: 100 wt.% CuScrap (Scrap), a mix of 50 wt.% CuScrap and 50 wt.% WPCBs (Mix), and 100 wt.% WPCBs (PCB). Life cycle assessment (LCA), focused on greenhouse gas emissions (Global Warming Potential), was conducted using OpenLCA software and the Ecoinvent 3.8 database to evaluate environmental impacts. The CO_2 emission results showed that recycling of copper from copper scrap causes the lowest emissions, but recycling PCBs also produces precious metals. Accordingly, a reduction in total emissions is achieved as these are distributed among the other valuable metals. Refer to exergetic assessment, the highest exergy loss is observed in the Smelter (Reducer) unit among all the cases. The losses ranges from 28.48% to 61.19%, indicating significant inefficiencies in energy utilization during reduction process. Particularly noteworthy is the PCB case, where the exergy loss reaches its peak of 61.19%, highlighting substantial energy wastage. It is mainly due to the presence of plastics in the WPCBs.

Based on modelling of individual steps and consideration of processing networks, it was possible to compute environmental impacts for the investigated processes and materials. The LCIA mid-point assessment results revealed higher impact of bronze than brass in different categories (such as resource depletion, climate change, and greenhouse gas emissions). The major reason is the presence of 12 wt.% of tin bronze and tin inherently has more environmental impacts than zinc. For instance, tin has 50% more GHG emissions than that of zinc. Moreover, both bronze and brass production showed minimal impact on abiotic depletion, acidification, eutrophication, photochemical oxidation, and ozone layer depletion. The aforementioned findings underscores the importance of considering environmental implications of technologies being used in the production process along with the use of energy sources, particularly in light of efforts to mitigate climate change and promote sustainability.

Moreover, variations of the GWP results noticed in all the studied cases, with bronze production generally exhibiting higher impacts *i.e.* 33.46%, 32.33%, and 32.41% for Scrap, Mix, and PCB cases, respectively, as compared to brass production due to the presence of tin (in bronze) which exhibits 3.7

times higher emissions than zinc (present in brass). Overall, the results showed that it is possible to store and track material and its production impacts through multiple process steps based on the processes described by an ontology and assignable impacts. The ontology research has been conducted with the collaboration of Fraunhofer Institute fur Werkstoffmechanik (IWM), Freiburg, Germany.

Teil II: Eingehende Darstellung (wird veröffentlicht)

Work package 1.

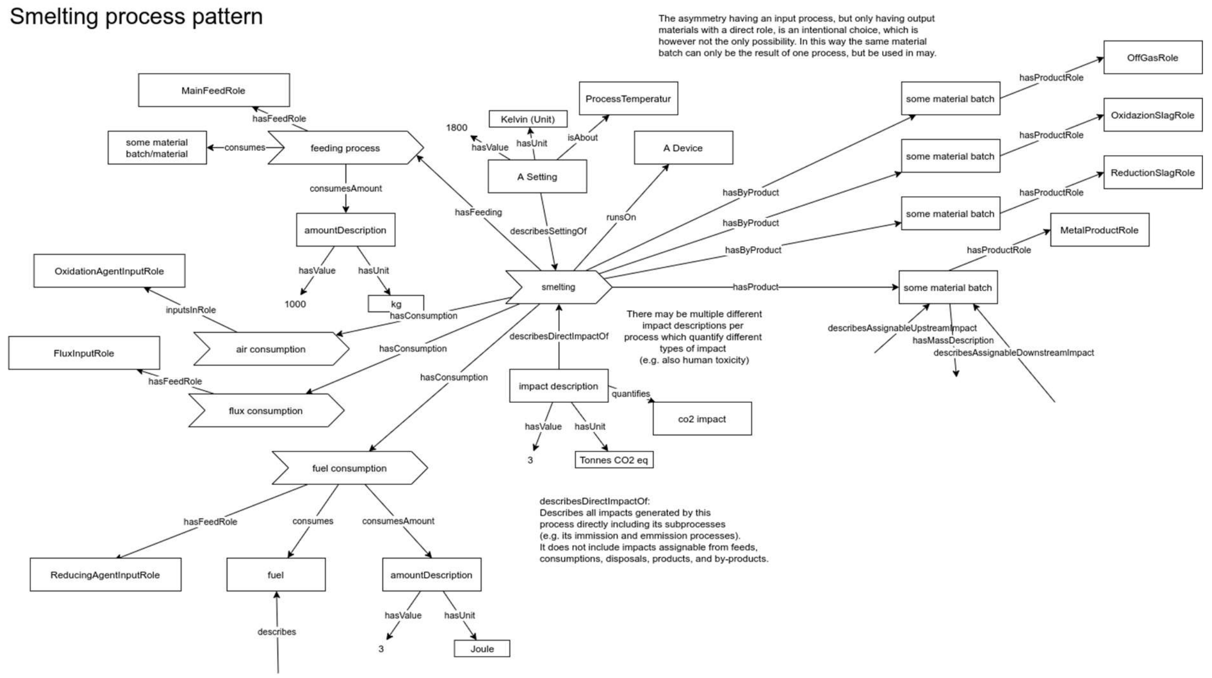
In work package 1.1, the central challenge of the ontology development for the primary production and recycling of copper were revealed: Production and Recycling of copper always interacts with the processing chains of other various materials. Considering various by-products in primary production or the fact that it is possible to completely recycle copper from products which contain many other elements alongside copper or a single copper alloy. Any ontology describing this process good enough to fulfil basic competences like relevantly describe environmental impacts associated to the production processes thus need to handle not only the copper production chain, but also to be standardized among a whole ecosystem of processing many different raw materials, including required chemicals and by-products as well as for disposing of wastes generated from the process. This initially asked for using standard ontologies for describing the networks. However, the competence analysis again showed that standard approaches of process description, e.g. those based on EMMO or BFO, were not powerful enough to describe processing networks in a way competent enough to answer questions relevant to environmental impacts assignable to each products of a complex network. It was also detected that unlike in the other fields of the KupferdDigital Project, where very clearly defined processes needed an ontology, which describe repetitive processes with a focus on providing the data (e.g. the copper production and recycling comes in infinitely many variations), and the ontology is needed to describe the structure of process, rather than only its parameters.

In work package 1.2, we therefore developed a proposal for an ontology which is capable of describing complex raw materials processing networks independent of raw material production specifically and is able to express the interdependencies of a complex processing network for various relevant disciplines including processing engineering design and environmental impact assessment.

This part of the ontology is explained mainly in the publication Mohsin Sajjad, Karl Gerald van den Boogaart, Leon Steinmeier, and Ashak Mahmud Parvez (2024), **Environmental Impact Assessment of Copper-Alloy Production Using Process Simulation and Semantic Modelling**, *Advanced Engineering Materials*. 2024, 240170.

https://doi.org/10.1002/adem.202401702

The following diagram exemplifies graphically how the ontology would be used for a smelting process with multiple inputs and outputs with a simplified and cropped example.


Smelting process pattern

The asymmetry having an input process, but only having output materials with a direct role, is an intentional choice, which is however not the only possibility. In this way the same material batch can only be the result of one process, but be used in may.

There may be multiple different impact descriptions per process which quantify different types of impact (e.g. also human toxicity)

describesDirectImpactOf:
Describes all impacts generated by this process directly including its subprocesses (e.g. its immission and emmission processes).
It does not include impacts assignable from feeds, consumptions, disposals, products, and by-products.

Figure 1: Semantic description of impacts of processes.

Since this ontology could not be designed specifically for copper but rather applies to a much wider range of material processing and also substantially differs in structure and mode of application from the ontologies developed for the other parts of the copper cycle, it was not reasonable to integrate into the copper specific ontology published by KupferdDigital. As general ontology also applying to other raw materials value chains, it is also not something that could be finalized and put out as a standard by a consortium exclusively focusing on copper. It was thus provided as a draft on the git-lab repository of published ontology, and discussed as a draft in a publication, such that it can be used with the published ontology to describe the whole copper cycle, but requiring further community development that was not included in the ontology itself.

In work package 1.3, we checked that the ontology interacts well with the other sub ontologies provided, since it interacts indirectly by describing types, batches and streams of material from the perspective of their production, environmental impact, and use rather from the standpoint of their characterization. The ontology can thus be fully integrated in used cases without the requirement of a direct connection on the ontology level.

Due to the complexity and flexibility of this open approach, which does not limit the description to specific materials, or specific processes, it was however not possible to develop automated quality tests in work package 1.4 for this part of the ontology. Manual competence checks however showed that various different questions can be answered for data provided complex process networks based on this description. An open question is how the system behaves if the same process is described on multiple different levels of detail in the same graph.

Work package 2.1 (Datenökosystem/Anforderungsanalyse).

Multiple requirements for a data ecosystem for handling processing data including environmental impacts have been identified:

- Integration of data from producers and disposal data along the whole processing network. I.e. an integrated dataspace collecting data from all relevant stakeholders is required.
- Here a part of the data, like the exact methods of processing, might be confidential, while other parts, like the proclaimed environmental impacts assignable to intermediate products, are required at least direct customers to provide similar data to their customers. I.e. an industrial dataspace with granular and contract based access control is required.
- Computations require to see data from different stakeholders. I.e. the dataspace needs to provide access to algorithms, to compute information in a reliable way, on data which might be confidential.

In conclusion, the recycling and processing specific data again calls for an industrial dataspace, like also all other parts of the project carried out.

Work package 3.6 (process model development)

Within the scope of work package 3.6, process model and simulation of two alloys has been developed at three cases (e.g. Cu Scrap, WPCBs and mixed of Cu Scrap and WPCBs). Accordingly, six simulation flow-sheets were developed in this work package aiming the production of copper alloys using two types of secondary copper resources. The detail methodology and achieved results are given below:

Feed material:

This study uses two distinct types of copper-rich waste (CuScrap and WPCBs) which are assumed to be the representative of WEEE. The properties of these materials are outlined as follows:

CuScrap: This material typically comprises approximately 75 wt.% copper with minimal impurities. It was assumed that about 3-4 wt.% of the composition of CuScrap consists of oxides, primarily in the form of Cu_2O. The composition estimation was sourced from the Institute of Scrap Recycling Industries (ISRI) [1]. The selected CuScrap composition represents post-production scrap commonly found in industrial recycling streams. Table 1 provides a breakdown of the composition.

Table 1. Copper scrap composition

Copper scrap (wt.%)						
Total Metallic	**Cu**	**Cu_2O**	**Sn**	**Pb**	**Zn**	**Ni**
100%	73	3.5	3	5	15	0.5

WPCBs: WPCBs exhibit the most intricate and diverse composition among Waste Electrical and Electronic Equipment (WEEE) [2]. Their copper content generally varies from 7-22 wt.%. This variability presents a challenge in obtaining precise results, as defining a consistent composition for WPCBs remains a limitation. Additionally, WPCBs contain significant quantities of precious metals like gold (Au) and silver (Ag), as well as critical metals such as palladium (Pd), tantalum (Ta), and cobalt (Co). Table 2 provides an overview of the representative composition of WPCBs considered in this study.

Table 2. Waste PCBs composition

Waste PCBs (wt.%)												
Total Metallic	Cu	Fe	Al	Sn	Pb	Ni	Zn	Ag	Au	Pd	Ta	Co
40%	22	6	4	3	3	1	0.8	0.1	0.04	0.02	0.02	0.02
Total Plastic	C_3H_6	C_2F_4	C_2H_6	C_2H_3Cl	$C_{10}H_{20}O_2$	$C_{15}H_{16}O_2$	$C_{12}H_{22}O_4$					
30%	5	2	10	2	5	5	1					
Total Ceramic	SiO_2	MgO	Al_2O_3	CaO	K_2O	Na_2O	TiO_2					
30%	15	2	6	1	1	2	3					

In this study, three distinct cases were examined, each based on the composition of the feed material. The studied cases are as follows: **Case 1**, referred to as Scrap, utilized a feed rate of 20 tons per hour (t/h) of CuScrap without WPCBs. **Case 2,** referred to as Mix, included a feed rate of 10 t/h of CuScrap combined with 10 t/h of WPCBs. Finally, **Case 3**, denoted as PCB, involved a feed rate of 20 t/h of WPCBs with no CuScrap.

FactSage and HSC Sim Simulation:

The amounts of feeds, consumables, products, by-products, and direct impacts of each process need to be measured or calculated. One way of doing this is through simulation. The three cases mentioned earlier were evaluated under the traditional scenario where conventional fuels (i) coke was used for reduction and oxidation, while (ii) natural gas was used in fire refining and crucible furnace [3].

The study employed HSC Sim [4] and FactSage [5] software with specific phases: (Fact PS) for the gas phase, (FToxid-SLAGA) for the slag phase, and (FScopp-Liqu) for the metal phase. These software tools were employed to model the secondary copper production process and subsequently the production of copper alloys *i.e.* bronze and brass by using tin and zinc, respectively. Table 3 shows the operational parameters (*i.e*. temperature, partial pressure of oxygen (ppO_2)), inputs, and outputs of all the pyrometallurgical processes. These parameters were adopted from thermodynamic [6], industrial [7] and experimental data [8] in the studied simulation.

Figure 2 presents the HSC Sim flowsheet for the production of bronze and brass. The proposed methodology follows a sequence of operations based on the well-known black copper route for secondary copper production. This route begins with a shredding process to prepare the material (as per the earlier mentioned cases) for feeding the smelter. It then moves to the smelter-reducer, followed by the converter-oxidizer stage. The material is then subjected to fire-refining, anode casting, and finally, electro refining to achieve a copper cathode with a copper purity level of 99.99 wt.% Cu. These stages involve the feed material at high temperature (1300 °C) and under reduced partial pressure of oxygen (*i.e.* ppO_2 of 10^{-8} atm) using coke, enriched oxygen, along with the presence of fluxing agents, such as FeO, CaO and SiO_2. The purpose of smelter-reducer is to achieve a 80% Cu content in black copper as well as 1 wt.% of Cu_2O in slag. Moreover, the converter-oxidizer, follows the smelter-reducer and focuses on the oxidation of impurities present in the black copper at (1300 °C), under a ppO_2 of 10^{-5} atm, to obtain rough copper with a Cu content of 96–97 wt.%. The converter-oxidizer utilizes coke as a fuel and fluxing materials such as FeO, CaO, and SiO_2, to facilitate slag formation. During fire refining, impurities in the rough copper (i.e. Fe, Sn, Pb, and other minor elements) gets segregated into the slag phase with the help of fluxing agents through high-temperature of 1200 °C and ppO_2 of 10^{-6} atm. The fire refining process uses natural gas as a fuel and the achieved product so called anode copper is 98.5 to 99.5 wt.% enriched in copper. In the casting stage, the molten copper is carefully poured into mold to form anodes.

Table 3: Input, output, and operational parameters of the pyrometallurgical units used in FactSage simulation.

		Reduction							**Oxidation**							**Fire Refining**						
		Literature	This study (conv.)			This study (Hydrogen)			Literature	This study (conv.)			This study (Hydrogen)			Literature	This study (conv.)			This study (Hydrogen)		
	Unit		Scrap	Mix	WPCB	Scrap	Mix	WPCB		Scrap	Mix	WPCB	Scrap	Mix	WPCB		Scrap	Mix	WPCB	Scrap	Mix	WPCB
Operational parameters																						
Temperature	ºC	1200–1400	1300	1300	1300	1300	1300	1300	1200–1400	1300	1300	1300	1300	1300	1300	1200 – 1300	1300	1300	1300	1300	1300	1300
ppO_2	atm	10^{-7}–10^{-9}	10^{-9}	10^{-9}	10^{-9}	10^{-9}	10^{-9}	10^{-9}	10^{-5}–10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6} – 10^{-7}	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}	10^{-6}
Input																						
Air	t/h		0.07	16	35	0.01	16	34		2.95	2.5	2.5	3.15	2.5	3.0		8.24	5.2	6.3	5.37	6.0	4.1
Coke/H_2/NG	t/h		0.22	0	0	0.095	0	0		0.2	0.2	0.23	0.04	0.14	0.11		0.38	0.24	0.31	0.12	0.14	0.1
Flux	t/h		0	0	4.54	0	0	9		8.61	7.0	4.9	9.11	7.0	4.2		4.98	3.13	1.31	4.7	4.3	1.6
Output																						
		Black Copper							**Rough Copper**							**Anode Copper**						
Cu	wt.%	74 – 85	78.3	81.4	75.5	80.2	79.7	75.6	95 – 97	96.5	96.4	96.3	96.9	95.3	96.1	>98	98.3	97.6	98.0	98.4	98.1	97.6
Sn	wt.%	6 – 8	9.8	10.6	16.1	8.2	11.7	15.6	-	1.19	1.82	1.78	1.23	1.55	1.84	-	1.03	0.87	0.41	0.88	0.36	0.62
Pb	wt.%	5 – 6	5.9	3.4	1.2	6.2	3.0	1.3	-	1.49	0.04	0.04	1.11	0.85	0.04	-	0.06	0.00	0.09	0.14	0.05	0.00
Zn	wt.%	1 – 3	1.7	1.2	0.03	1.2	1.6	0.04	-	0.00	0.00	0.00	0.00	0.01	0.00	-	0.00	0.00	0.00	0.00	0.00	0.00
Ni	wt.%	1 – 3	1.0	2.2	5.5	1.2	2.0	5.6	-	0.64	1.46	1.09	0.53	1.00	1.19	-	0.48	1.13	0.73	0.53	0.30	0.92
Fe	wt.%	5 – 8	3.2	1.1	1.2	2.9	1.9	1.4	-	0.18	0.17	0.11	0.13	0.11	0.12	-	0.17	0.21	0.10	0.06	1.06	0.06
O	wt.%	-							-							<0.3	0.27	0.3	0.28	0.27	0.2	0.14
Slag																						
Cu_2O	wt.%	0.6 – 1	0.7	0.97	0.7	0.7	0.94	0.8	10 – 30	11.3	16.8	22.0	17.5	12.1	20.6	-	13.83	12.02	20.17	16.37	15.49	10.88
SnO	wt.%	0.5 – 0.8	2.3	0.97	0.9	2.7	2.7	1.2	5 – 15	10.7	10.5	13.5	8.7	11.2	13.1	-	0.68	3.05	4.01	1.24	2.72	3.25
PbO	wt.%	-	3.90	0.01	0.01	3.80	0.01	0.01	5 – 15	5.1	3.4	1.0	5.8	1.3	1.0	-	1.97	0.05	0.03	0.95	0.35	0.03
ZnO	wt.%	3.5 – 4.5	19.0	4.3	0.7	18.7	6.4	0.5	3 – 6	2.1	1.4	0.03	1.5	1.6	0.04	-	0.00	0.00	0.00	0.00	0.02	0.00
NiO	wt.%	-	0.18	0.29	1.04	0.12	0.87	0.82	1 – 5	0.9	1.7	5.5	1.1	2.0	5.2	-	0.64	1.34	1.44	0.13	1.84	0.98
Off-gas																						
CO_2	t/h	-	0.61	7.18	15.3	0	6.84	14.8	-	0.64	0.65	0.75	0	0	0	-	1.02	0.64	0.84	0	0	0
CO	t/h	-	0.26	0.46	0.35	0	0.97	0.90	-	0.01	0.01	0.01	0	0	0	-	0.01	0.01	0.01	0	0	0
HF	t/h	-	0	0.16	0.32	0	0.17	0.33	-	0	0	0	0	0	0	-	0	0	0	0	0	0
HCl	t/h	-	0	0.12	0.23	0	0.12	0.24	-	0	0	0	0	0	0	-	0	0	0	0	0	0

The last step of secondary copper production involves electrolytic refining, which employs an electrolytic cell, typically consisting of an electrolyte solution at 64 °C, containing 170–200 g/L H_2SO_4 and two electrodes: the anode (made of the casted copper anodes) and the stainless steel cathode. The objective of electrolytic refining is to further purify the Cu obtained from previous stages and achieve an extremely high level of Cu purity, often reaching 99.99 wt.%, it also separates valuable impurities such as Au, Ag and Pd to recover them as by products. Once 99.99 wt.% copper is obtained, it is mixed with pure tin at 1000 °C or zinc at 950 °C separately in a crucible furnace to produce bronze or brass, respectively. Similar to fire refining, crucible furnace also uses natural gas as a fuel. The processes for the production of bronze and brass were similar until the production of copper cathodes, however, the crucible furnace was modelled separately for both of the alloys, and hence generalized flowsheet is shown in Figure 2.

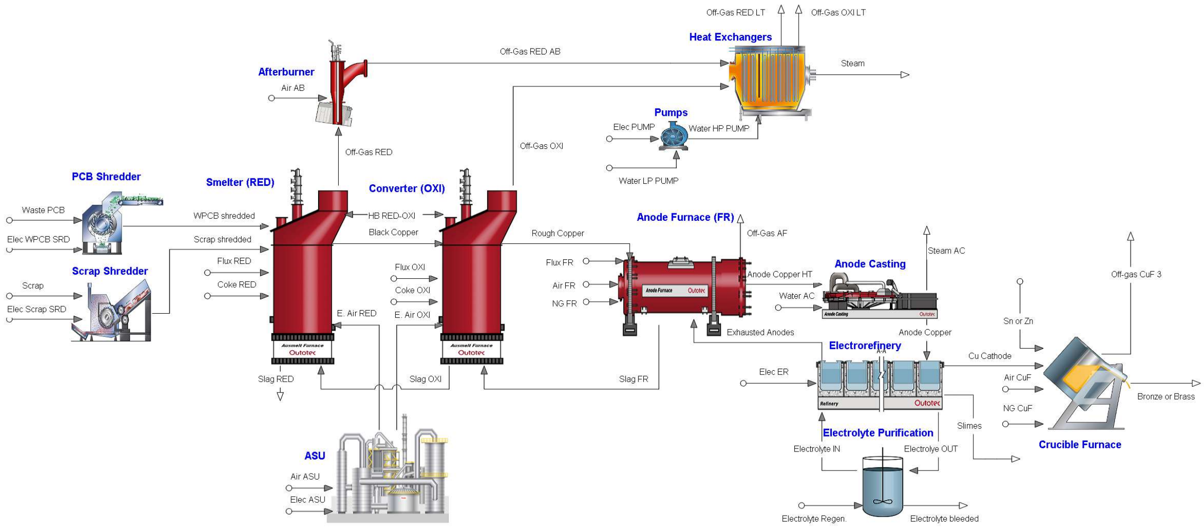


Figure 2. HSC Sim simulation flowsheet of Cu-alloy production

Life cycle assessment:

Life cycle assessment (LCA) serves as a method for comprehensively analyzing the environmental aspects and potential impacts of a product or service, considering its entire lifecycle, spanning from creation to disposal. According to the ISO 14040 standard, the LCA process encompasses four key stages: establishing the goal and scope, compiling a Life Cycle Inventory (LCI) as well as a life cycle impact assessment (LCIA), and interpreting the findings. In-depth information regarding these stages is available in literature [9]. For the LCA, OpenLCA 1.10.0 software including Ecoinvent 3.8 database was used.

Goal and Scope

The goal of this comprehensive LCA was to quantitatively evaluate the environmental impacts associated with the production of bronze and brass. The functional unit will be evaluated as the amount of kg of bronze and brass. This aspect holds significant importance in the LCA study, as the results will be presented in relation to the chosen functional unit. As illustrated in Figure 3, the boundary conditions for the LCA was established employing a Gate-to-Gate approach. As mentioned earlier (section 2.2), the processes for the production of bronze and brass were similar until the production of copper cathodes, however, the crucible furnace was modeled separately for both, the bronze and brass using tin and zinc, respectively. Therefore, the boundary conditions shown in Figure 3 were also kept separate in LCA for the respective alloy.

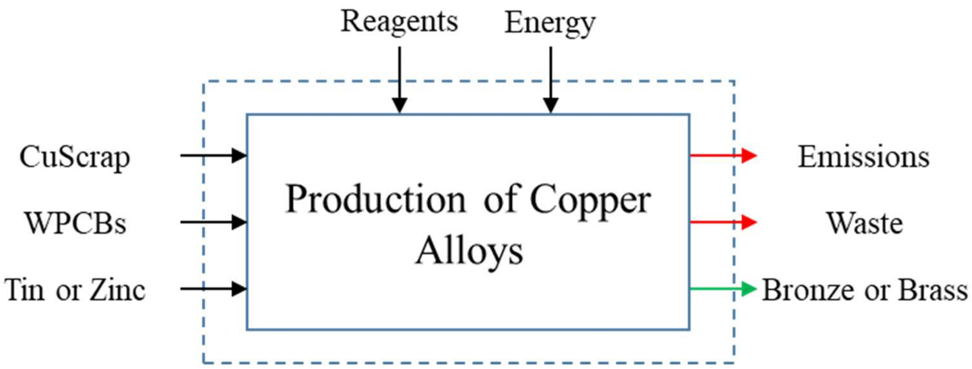


Figure 3. LCA system boundary (black arrows: inputs; red arrows: emissions, and green arrows: products)

Life Cycle Inventory

In conducting the life cycle inventory (LCI), the Ecoinvent 3.8 database was utilized. Herein, Reagents Energy, Emissions, and Waste were categorized as techno sphere and elementary flows, while the feed materials were constituted as an intermediate flows, and bronze and brass were represented as the product flows. According to [9], this process involves compiling and quantifying input and output data within the defined system boundary, accounting for the movement of materials, energy, waste, and resources. The data is specific to the functional unit, encompassing the energy and materials required for it, as well as the resulting emissions and waste generation. Table 4 presents the life cycle inventory.

Table 4. Selected inventory results, inputs and outputs per kg of bronze and brass

		Scrap		Mix		PCB	
Inputs	**Unit**	**Bronze**	**Brass**	**Bronze**	**Brass**	**Bronze**	**Brass**
calcined clay	kg	0.056	0.043	-	-	0.163	0.124
coke	MJ	0.700	0.539	0.519	0.395	1.356	1.033
copper scrap, sorted, pressed	kg	1.190	0.917	0.928	0.706	-	-
electricity, medium voltage	kWh	0.377	0.290	0.552	0.420	1.235	0.940
iron scrap, sorted, pressed	kg	0.439	0.338	0.564	0.429	1.212	0.923
natural gas, medium pressure, vehicle grade	kg	0.045	0.039	0.050	0.039	0.128	0.099
nitrogen	kg	0.830	0.697	1.808	1.387	6.173	4.724
oxygen	kg	0.197	0.167	0.251	0.194	0.597	0.461
oxygen, liquid	kg	0.090	0.069	0.863	0.657	3.928	2.991
printed circuit boards waste	kg	-	-	0.928	0.706	4.213	3.207
silica sand	kg	0.313	0.241	0.376	0.286	0.885	0.674
sulfuric acid	kg	0.063	0.049	0.072	0.055	0.066	0.050
tin	kg	0.119	-	0.120	-	0.120	-
water, unspecified natural origin, DE	m^3	5.0E-04	3.8E-04	1.4E-03	1.1E-03	4.5E-03	3.4E-03
zinc	kg	-	0.321	-	0.330	-	0.330
Outputs							
aluminium oxide, fibrous forms	kg	5.0E-04	3.8E-04	0.086	0.065	0.388	0.295
carbon dioxide, fossil	kg	0.205	0.169	0.929	0.709	3.839	2.927
carbon monoxide	kg	1.3E-03	1.0E-03	0.002	0.001	0.003	0.002
cobalt oxide	kg	-	-	2.3E-04	1.7E-04	1.1E-03	8.1E-04
copper oxide	kg	0.008	0.006	0.014	0.011	0.033	0.025
copper sulfate	kg	0.041	0.031	0.041	0.031	0.041	0.031
gold, unrefined	kg	-	-	3.7E-04	2.8E-04	1.6E-03	1.2E-03
hydrogen fluoride	kg	-	-	0.026	0.020	0.117	0.089
Iron II	kg	0.407	0.314	0.557	0.424	1.201	0.914

Iron III	kg	0.034	0.026	0.085	0.065	0.374	0.285
lead compounds	kg	0.047	0.036	0.081	0.061	0.135	0.103
nickel compounds	kg	0.013	0.010	0.031	0.024	0.063	0.048
palladium	kg	-	-	1.8E-04	1.4E-04	8.4E-04	6.4E-04
silver, unrefined	kg	-	-	9.2E-04	7.0E-04	4.2E-03	3.2E-03
steam, in chemical industry	kg	0.352	0.272	0.457	0.348	4.364	3.322
sulfur dioxide, DE	kg	4.6E-04	3.6E-04	2.9E-04	2.2E-04	7.7E-04	5.9E-04
sulfuric acid	kg	0.030	0.023	0.030	0.023	0.029	0.022
tin oxide	kg	0.004	0.003	0.041	0.031	0.101	0.077
waste water	m^3	2.5E-04	2.0E-04	5.7E-04	4.3E-04	1.8E-03	1.4E-03

Table 5 shows all the providers of energy and resources used in the overall process in Ecoinvent to link the LCI in OpenLCA.

Table 5. Energy and resources provider

Energy and Resources	Provider
Electricity	Electricity, medium voltage APOS, S – NO
Coke	Market for coke APOS, S – GLO
Oxygen	Market for oxygen, liquid | oxygen, liquid | APOS, S - RER
Flux:	FeO, CaO, and SiO_2
FeO	Market for iron scrap, sorted, pressed APOS, S - RER
CaO	Market for calcined clay APOS, S - RoW
SiO_2	Market for silica sand APOS, S – GLO
Natural gas	Market for natural gas, medium pressure APOS,S – GLO
Sulfuric acid	Market for sulfuric acid APOS, S – RER
Tin	Market for tin | tin | APOS, S – GLO
Zinc	Market for zinc | zinc | APOS, S - GLO

Life Cycle Impact Assessment

In conducting the life cycle inventory (LCI), the Ecoinvent 3.8 database was utilized. Herein, Reagents Life-Cycle Impact Assessment (LCIA) involves considering factors such as resource consumption, emissions, and waste generation. The initial step involves selecting impact categories, indicators, and characterization models. The subsequent stage involves categorizing individual flows based on the impact categories they contribute to. Finally, characterization factors are applied to these categorized elementary flows, yielding quantifiable values for comparison. The midpoint approach scrutinizes effects occurring in the middle of the causality chain. The ReCiPe method is used in LCIA calculations, assigning impact scores to various emissions through characterization factors. These factors can be determined using two primary methods: at the midpoint or endpoint levels. ReCiPe provides calculations for both, 18 midpoint indicators and 3 endpoint indicators.

Interpretation of the results

In accordance with [9], the final phase encompasses interpretation. Here, the results of both LCI and LCIA are summarized and deliberated, considering the defined goal, scope, limitations, and sensitivity analysis within the copper alloys production process.

Results and Discussion:

Mass balance

In conducting LCA of the bronze and brass production process, detailed inventory for the copper cathodes was used from the HSC and FactSage simulations. However, for tin and zinc, the Ecoinvent 3.8 database was used for their respective providers listed in Table 5. Table 6 compares the GHG emission results from previous LCA studies on copper, tin, and zinc with those from this study. However, the comparison shows that for copper production, GWP estimation ranges around 2.5 to 0.32 kg CO_2 eq./ kg copper for primary and secondary copper production processes, respectively. From the current study, the GWP estimation obtained from the simulation of secondary copper production process is 0.38 kg CO_2 eq./ kg copper, which agrees well with the previous studies within a reasonable limit. Similarly for zinc, the comparison shows that GWP estimation ranges around 3.1 to 2.6 kg CO_2 eq./ kg zinc and the GWP estimation obtained from Econinvent database is 2.7 which also agrees well with literature. However, for the case of tin, the GWP estimation ranges from 17.1 to 1.61 kg CO_2 eq./ kg tin for primary and secondary tin production processes, respectively while the Ecoinvent database value is 10.1 kg CO_2 eq./ kg tin. The difference in estimates can be attributed to the research scope, system boundary, analysis method, geographic region consideration, allocation technique, energy mix, and heat mix vary among the studies, even though the studies were conducted for the same metal.

Table 6. Comparison of results.

Metal	This study	Literature	Reference
Copper	0.38 kg CO_2 eq./ kg[a]	2.5 kg CO_2 eq./ kg (primary production)	Memary et al. [10]
		0.32 kg CO_2 eq./ kg (secondary production)	Dong et al. [11]
Tin	10.01 kg CO_2 eq./ kg	17.1 kg CO_2 eq./ kg (primary production)	Nuss and Eckelman [12]
		1.61 kg CO_2 eq./ kg (secondary production)	Aurubis [13]
Zinc	2.70 kg CO_2 eq./ kg	3.1 kg CO_2 eq. /kg	Nuss and Eckelman [12]
		2.6 kg CO_2 eq. /kg	Genderen et al. [8]

[a] For the Mix case

The mass balance of the material flow was calculated to gain a better understanding of the accuracy of the LCIA results. For instance, the initial values for the production of bronze using CuScrap as feed material were 20 tons of CuScrap, 0 tons of WPCBs, 2 tons of primary tin, 0 tons of primary zinc, and 45.9 tons of other raw materials (e.g. coke, natural gas etc.). In contrast, the output values were 16.8 tons of bronze, 0 tons of by-products (i.e. gold, silver, and palladium during the production of copper cathodes), and 50.4 tons of waste (e.g. slags, off-gases etc.). The loss rate was approximately 1%, indicating a high degree of inventory reliability in the LCI listed in this study had, as shown in Table 7. Measurement error and missing inventory data were possibly responsible for the mass loss.

Table 7. Mass balance of bronze and brass production processes

			Scrap		**Mix**		**PCB**	
		Unit	**Bronze**	**Brass**	**Bronze**	**Brass**	**Bronze**	**Brass**
Input	copper scrap	ton	20.0	20.0	10.0	10.0	-	-
	printed circuit boards	ton	-	-	10.0	10.0	20.0	20.0
	primary tin	ton	2.0	-	1.3	-	0.6	-
	primary zinc	ton	-	7.0	-	4.7	-	2.1
	raw materials	ton	45.9	47.6	48.5	48.7	68.9	69.1
	Total	ton	67.9	74.6	69.8	73.4	89.5	91.1

Output	product	ton	16.8	21.8	10.8	14.2	4.7	6.2
	byproducts	ton	-	-	1.6E-02	1.6E-02	3.2E-02	3.2E-02
	waste	ton	50.4	52.0	58.1	58.2	83.7	83.8
	Total	ton	67.2	73.8	68.9	72.4	88.5	90.1
	Loss rate	%	1.1%	1.0%	1.3%	1.4%	1.0%	1.2%

Exergy Analysis

The incoming and outgoing exergy values for all the unit processes involved in the production of bronze and brass, along with the percentage loss of exergy are presented in Table 8. The highest exergy loss is observed in the "Smelter (Reducer)" across all cases: Scrap, Mix, and PCB cases. The losses ranges from 28.48% to 61.19%, indicating significant inefficiencies in energy utilization during reduction process. Particularly noteworthy is the PCB case, where the exergy loss reaches its peak of 61.19%, highlighting substantial energy wastage. It is mainly due to the presence of plastics in the WPCBs. A comparable study by [14] reported an exergy loss of approximately 44.79% for the reduction process in the Mix case.

Looking at the overall process, which includes all unit processes involved in bronze and brass production, the exergy losses range from 13.90% to 30.58%. These losses signify inefficiencies in the entire production chain, with higher losses observed in cases involving WPCBs.

Table 8. Exergy flow rates of process units in bronze and brass production

			Scrap		**Mix**		**PCB**	
		Unit	**Bronze**	**Brass**	**Bronze**	**Brass**	**Bronze**	**Brass**
Shredding	Input	kW	15,233.53	15,233.53	48,159.02	48,159.02	81,084.49	81,084.49
	Product	kW	14,241.93	14,241.93	47,224.52	47,224.52	80,207.09	80,207.09
	Loss	%	6.51%	6.51%	1.94%	1.94%	1.08%	1.08%
Smelter (Reducer)	Input	kW	25,974.81	25,974.81	54,686.40	54,686.40	87,535.01	87,535.01
	Product	kW	18,578.34	18,578.34	31,011.55	31,011.55	33,973.76	33,973.76
	Loss	%	28.48%	28.48%	43.29%	43.29%	61.19%	61.19%
Convertor	Input	kW	25,380.30	25,380.30	17,655.60	17,655.60	11,663.18	11,663.18

(Oxidizer)	Product	kW	22,666.42	22,666.42	15,563.72	15,563.72	9,301.14	9,301.14
	Loss	%	10.69%	10.69%	11.85%	11.85%	20.25%	20.25%
FireRefining	Input	kW	19,094.43	19,094.43	12,272.05	12,272.05	8,464.81	8,464.81
	Product	kW	16,595.50	16,595.50	10,663.12	10,663.12	6,023.80	6,023.80
	Loss	%	13.09%	13.09%	13.11%	13.11%	28.84%	28.84%
Electrorefining	Input	kW	9,082.06	9,082.06	5,878.31	5,878.31	2,542.33	2,542.33
	Product	kW	8,621.10	8,621.10	5,524.14	5,524.14	2,436.71	2,436.71
	Loss	%	5.08%	5.08%	6.02%	6.02%	4.15%	4.15%
Alloying	Input	kW	16,793.95	25,671.77	10,773.31	16,771.71	4,746.48	7,387.11
	Product	kW	14,668.36	22,998.10	9,411.10	15,036.83	4,146.33	6,622.91
	Loss	%	12.66%	10.41%	12.64%	10.34%	12.64%	10.35%
Overall Process	Input	kW	111,559.08	120,436.91	149,424.69	155,423.09	196,036.30	198,676.93
	Product	kW	95,371.65	103,701.39	119,398.15	125,023.88	136,088.83	138,565.42
	Loss	%	14.51%	13.90%	20.09%	19.56%	30.58%	30.26%

Life cycle impact assessment results

Table 9 shows LCIA mid-point assessment results, which indicate varying environmental impacts associated with the production of bronze and brass across different categories. Bronze production generally demonstrates higher values in all the categories to brass, suggesting a higher impact on resource depletion, climate change, and greenhouse gas emissions. The major reason is because of 12 wt.% of tin present in it and tin has more environmental impacts than that of zinc. For instance, in the case of GWP, it can be seen from Table 9 that the tin has 50% more GHG emissions than that of zinc. Moreover, both bronze and brass production show minimal impact on abiotic depletion, acidification, eutrophication, photochemical oxidation, and ozone layer depletion. This underscores the importance of considering the environmental implications of technologies used in the production processes along with the use of energy sources, particularly in light of efforts to mitigate climate change and promote sustainability.

Table 9. Selected impact assessment results, per kg of bronze and brass

		Scrap		Mix		PCB	
Category	**Unit**	**Bronze**	**Brass**	**Bronze**	**Brass**	**Bronze**	**Brass**
Abiotic depletion	kg Sb eq	3.21E-03	4.97E-04	3.23E-03	5.08E-04	3.23E-03	5.08E-04
Abiotic depletion (fossil fuels)	MJ	20.44	15.25	17.22	12.95	16.98	12.76
Acidification	kg SO$_2$ eq	1.36E-02	9.04E-03	1.26E-02	8.41E-03	1.25E-02	8.31E-03
Eutrophication	kg PO$_4$ eq	1.23E-02	5.20E-03	1.16E-02	4.67E-03	1.15E-02	4.60E-03
Fresh water aquatic ecotoxicity	kg 1,4-DB eq	11.63	5.27	10.44	4.40	9.92	4.00
Global warming	kg CO$_2$ eq	1.80	1.35	1.62	1.22	1.62	1.22
Human toxicity	kg 1,4-DB eq	17.26	10.67	18.42	11.53	17.89	11.12
Marine aquatic ecotoxicity	kg 1,4-DB eq	1.29E+04	1.29E+04	1.29E+05	1.01E+05	1.48E+05	1.16E+05
Ozone layer depletion	kg CFC-11 eq	1.12E-07	8.83E-08	8.95E-08	7.16E-08	8.77E-08	7.02E-08
Photochemical oxidation	kg C$_2$H$_4$ eq	4.85E-04	3.55E-04	4.00E-04	2.94E-04	3.89E-04	2.85E-04
Terrestrial ecotoxicity	kg 1,4-DB eq	1.60	1.23	0.39	0.30	0.08	0.06

Global Warming Potential

Global warming potential (GWP) serves as a crucial indicator for assessing the contribution of different processes to climate change, thus guiding the prioritization of mitigation efforts and the implementation of environmentally responsible practices within industries such as metal or alloy production. The contribution of each unit process involved in the production of bronze and brass to GWP are shown in Figure 4 and Figure 5, respectively. The emissions are categorized into two types (i) direct emissions, originating from processes such as bronze or brass furnace, electrorefining, anode casting, fire refining, converter-oxidizer, smelter-reducer, and shredding and (ii) indirect emissions, stemming from the production of tin, natural gas, electricity, acid, flux, coke, and enriched oxygen. These emissions are indicated in the legends with the suffixes D and ID, respectively. The adoption of economic allocation in LCIA is crucial, particularly in scenarios involving the recovery of precious metals like gold, silver, and palladium during copper production from Mix and PCB cases. In the bronze production scenario using Scrap, the highest impact is recorded at 1.796 kg CO$_2$ eq./ kg, while for the Mix and PCB cases, the impact stands at 1.617 kg CO$_2$ eq./ kg and 1.618 kg CO$_2$ eq./ kg, respectively. Similarly, in brass production from Scrap, the highest impact is observed at 1.346 kg CO_2 eq./ kg, whereas for the Mix and PCB cases, the impact is 1.222 kg CO_2 eq./ kg and 1.222 kg CO_2 eq./ kg, respectively. These results are difficult to compare with other studies due to the lack of such studies but separate comparison of the emission coming from copper, tin, and zinc was made and is shown in Table 6. Although Scrap case does not exhibit WPCBs and the WPCBs emits a lot of emissions due to the burning of plastics which consists of 30 wt.% of the WPCBs but still the GWP of Scrap case is higher than that of the other two studied cases. This is primarily due to the presence of precious metals like gold, silver, and palladium in WPCBs, where economic allocation allocate emissions based on their market value. It is known that the Mix case has half of the WPCBs as of the PCB case, which exhibit 100% WPCBs and means that the precious metals are present more in the PCB case and should share the burden of GWP more as compared with the Mix case. However, the Figure 4 and Figure 5 shows that the GWP of Mix and PCB cases is nearly the same. For instance, in the bronze production, the overall emissions are 1.617 kg CO_2 eq./ kg and 1.618 kg CO_2 eq./ kg for Mix and PCB case, respectively. This is because along with precious metals, PCB case exhibit more plastics, which are mainly the source of emissions in the reduction process (i.e. D: Reducer). Therefore, the direct emissions of the reducer are higher in the PCB case as compared with the Mix case. For instance, in the bronze production, the direct emissions of the reducer increases from 0.141 kg CO_2 eq./ kg to 0.165 kg CO_2 eq./ kg from the Mix case to the PCB case, respectively.

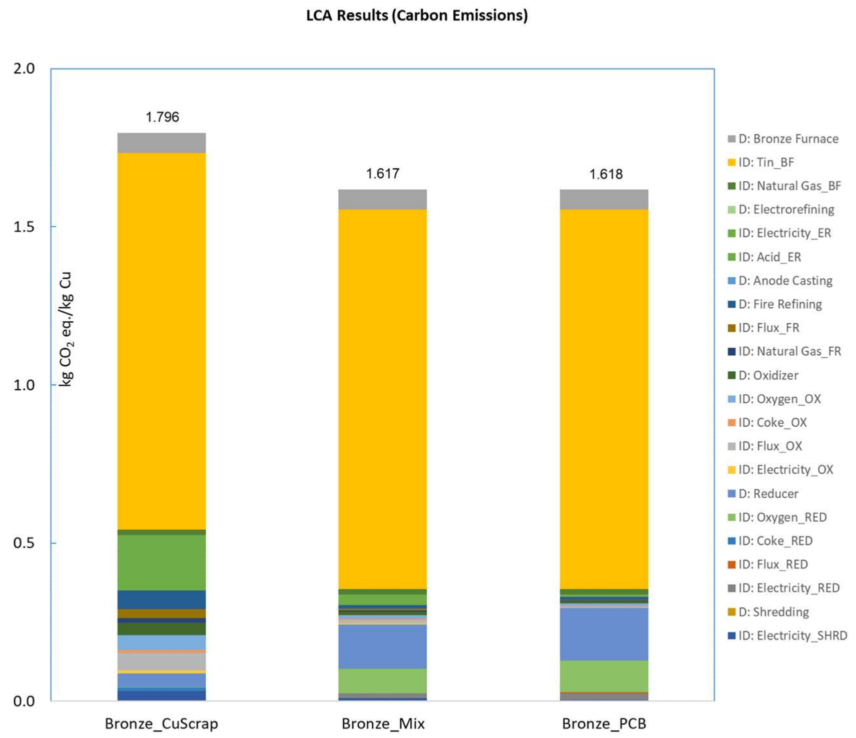


Figure 4. Contribution of process units to GWP per kg of bronze production

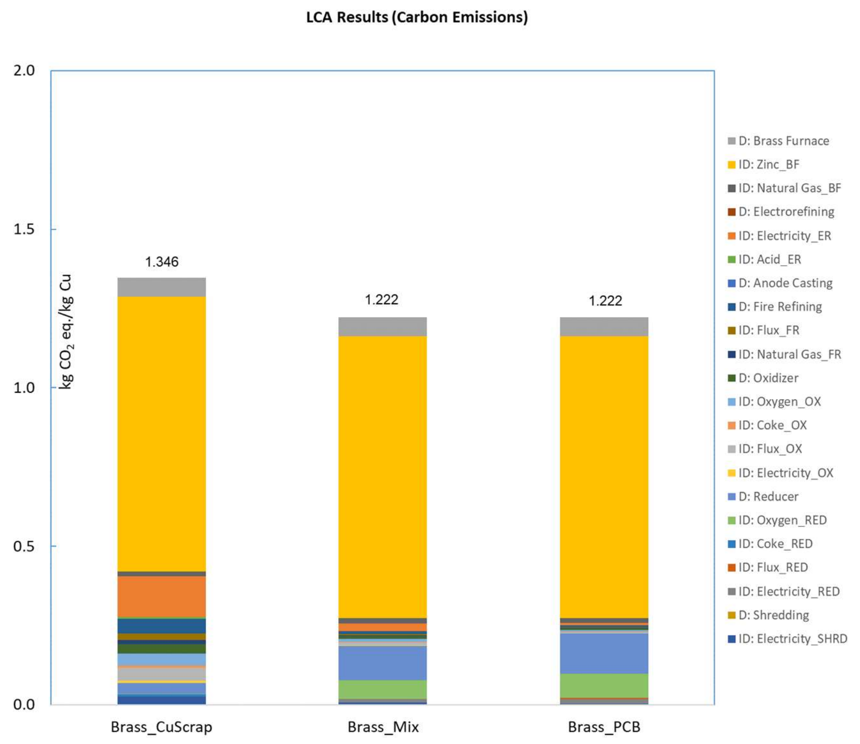


Figure 5. Contribution of process units to GWP per kg of brass production

Semantic embedding of life cycle assessment into process networks

In typical industrial situations not parts of a process are known in the beginning, but different companies have knowledge about and have access to different parts of a process chain. While impacts required for standard feed and consumables are typically available from standard LCA databases such as Ecoinvent, most of the other information is typically only available to individual stakeholders in the process, i.e. one person might be able to describe a process, including its feeds, products and its direct impacts, while a next person might be able to provide similar information for further steps, or downstream impacts of materials. The semantic approach allows collecting all this information separately, and computing remaining impacts by following the graph and using the relations.

Limitations and future perspective

This paper demonstrated how to compute, semantically express and propagate LCA impact data across complex raw materials process networks, with examples from copper production from secondary source.

While this study provides valuable insights into the environmental impact of bronze and brass production, certain limitations should be acknowledged. One limitation lies in the assumptions made regarding the composition and characteristics of feed materials, particularly WPCBs, which can vary significantly in composition and contamination levels. Furthermore, the analysis does not account for variations in production technologies and practices across different regions or facilities, which could significantly influence environmental performance. The semantic representations however allow to generalize the approach to more complex materials and process streams and allows combining information available to different stakeholders on a value chain.

Future research could address these limitations by conducting more detailed assessments of feed material compositions, incorporating additional environmental impact categories, and considering regional variations in production processes. Despite these limitations, this study offers valuable insights into potential strategies for reducing the environmental footprint of bronze and brass production. Moving forward, efforts to improve process efficiencies, increase the use of clean energy sources, and enhance recycling rates could help mitigate environmental impacts and promote sustainable production practices in the metal industry. Additionally, exploring innovative technologies and materials substitution could offer further opportunities for reducing environmental burdens associated with copper alloy production.

Conclusion

Semantic representation of process networks and their impacts provides a precise understanding of the environmental burdens generated across complex processing networks. The adopted approach allows all computations to be performed locally, relying solely on information from individual processes or products, either through simulation or through computations on the knowledge graph. This localized information can then be propagated step by step across the entire process network, facilitating collaboration between different stakeholders. Each stakeholder can focus specific parts of the graph and only needs to share impact data related to the common inputs and outputs. The present work further showed how environmental impact data, particularly related to greenhouse gas emissions, can be computed and stored semantically in the context of secondary copper production. The example provided a comprehensive assessment of the environmental impacts associated with producing bronze and brass using WPCBs as a secondary copper source. The findings revealed that secondary copper resources, especially WPCBs, significantly contribute to the overall environmental impact accounting for 10.21% of greenhouse gas emissions in the bronze production in PCB case, mainly due to the presence of plastics. The analysis also suggested that separating plastics from feed materials prior to processing could lead to a reduction in emissions. Additionally, optimizing process efficiencies, increasing the use of renewable energy sources, and enhancing recycling practices present valuable opportunities for reducing environmental impacts within the metal industry.

In this study, HSC Sim and FactSage software are employed to model and simulate the copper alloy production process from copper scrap (CuScrap) and waste-printed circuit boards (WPCBs) and an ontology to represent the results for individual process parts is developed in a way that impact assessment is possible for all materials in a complex process network. In the LCA results, variations across all the studied cases are indicated, with bronze production generally exhibiting higher impacts, i.e., 33.46%, 32.33%, and 32.41% for Scrap, Mix, and printed circuit board cases, respectively, as compared to brass production due to the presence of tin (in bronze) which exhibits 3.7 times higher emissions than zinc (present in brass).

References

[1] I. O. S. R. Industries, "ISRI Scrap Specifications Circular," July 2022. [Online]. Available: https://www.isrispecs.org/wp-content/uploads/2023/05/ISRI-Scrap-Specifications-Circular-updated-1.pdf. [Accessed 4 September 2023].

[2] A. Khaliq, M. Rhamdhani, G. Brooks and S. Masood, "Metal Extraction Processes for Electronic Waste and Existing Industrial Routes: A Review and Australian Perspective," *Resources,* vol. 3, no. 1, pp. 152-179, 2014.

[3] H. Lechtman and S. Klein, "The Production of Copper–Arsenic Alloys (Arsenic Bronze) by Cosmelting: Modern Experiment, Ancient Practice," *Journal of Archaeological Science,* vol. 26, no. 5, pp. 497-526, 1999.

[4] Outotec® HSC Chemistry® 10," [Online]. Available: https://www.metso.com/corporate/media/news/2020/1/outotec-hsc-chemistry-10/. [Accessed 09 October 2023].

[5] GTT-Technologies, "FactSageTM 2022.," [Online]. Available: https://gtt-technologies.de/software/factsage/. [Accessed 11 September 2023].

[6] J. Freudenberger, L. Tikana and W. Hosford , "Alloys: Copper," in *Encyclopedia of Condensed Matter Physics*, Second Edition ed., vol. Volume 5, Elsevier, 2024, pp. 601-634.

[7] M. Finkbeiner, A. Inaba and R. Tan, "The New International Standards for Life Cycle Assessment: ISO 14040 and ISO 14044," *Int J Life Cycle Assessment,* vol. 11, pp. 80-85, 2006.

[8] E. Van Genderen, M. Wildnauer, N. Santero and S. Nadir, "A global life cycle assessment for primary zinc production," *Int J Life Cycle Assess,* vol. 21, pp. 1580-1593, 2016.

[9] M. A. Curran, "Overview of Goal and Scope Definition in Life Cycle Assessment," in *Goal and Scope Definition in Life Cycle Assessment*, Netherlands, Springer, 2017.

[10] Memary, Reza; Giurco, Damien; Mudd, Gavin; Mason, Leah," *Life cycle assessment: a time-series analysis of copper,* vol. 33, pp. 97-108, 2012.

[11] D. Dong, L. van Oers, A. Tukker and E. van der Voet, "Assessing the future environmental impacts of copper production in China: Implications of the energy transition," *Journal of Cleaner Production,* vol. 274, p. 122825, 2020.

[12] P. Nuss and M. J. Eckelman, "Life Cycle Assessment of Metals: A Scientific Synthesis," *Plos One,* 2014.

[13] Aurubis, "Environmental Profiles of Our Products," December 2023. [Online]. Available: https://www.aurubis.com/en/responsibility/environment-energy-and-climate/ecological-footprint-of-our-products/environmental-profiles-of-our-products. [Accessed 15 March 2024].

[14] M. Ghodrat, B. Somali, M. A. Rhamdhani and G. Brooks, "Thermodynamic-Based Exergy Analysis of Precious Metal Recovery out of Waste Printed Circuit Board through Black Copper Smelting Process," *energies,* vol. 12, p. 1313, 2019.