Creating Wealth from Waste and Alternative Resources

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2nd Annual Symposium on Solid Waste Refinery, UGM

Yogyakarta, 13 November 2019

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Current Research Focus / Context

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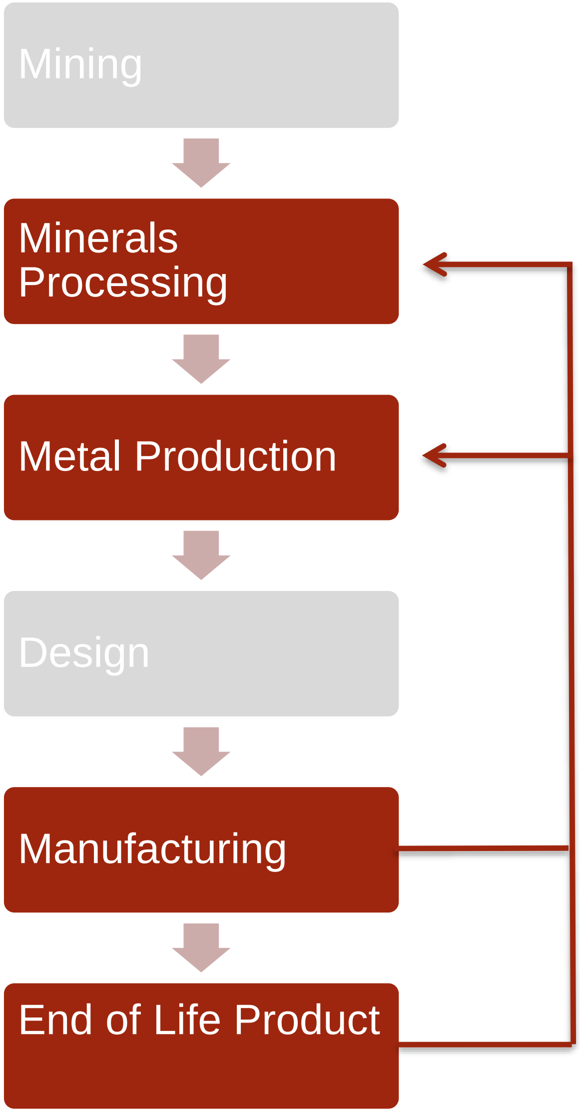
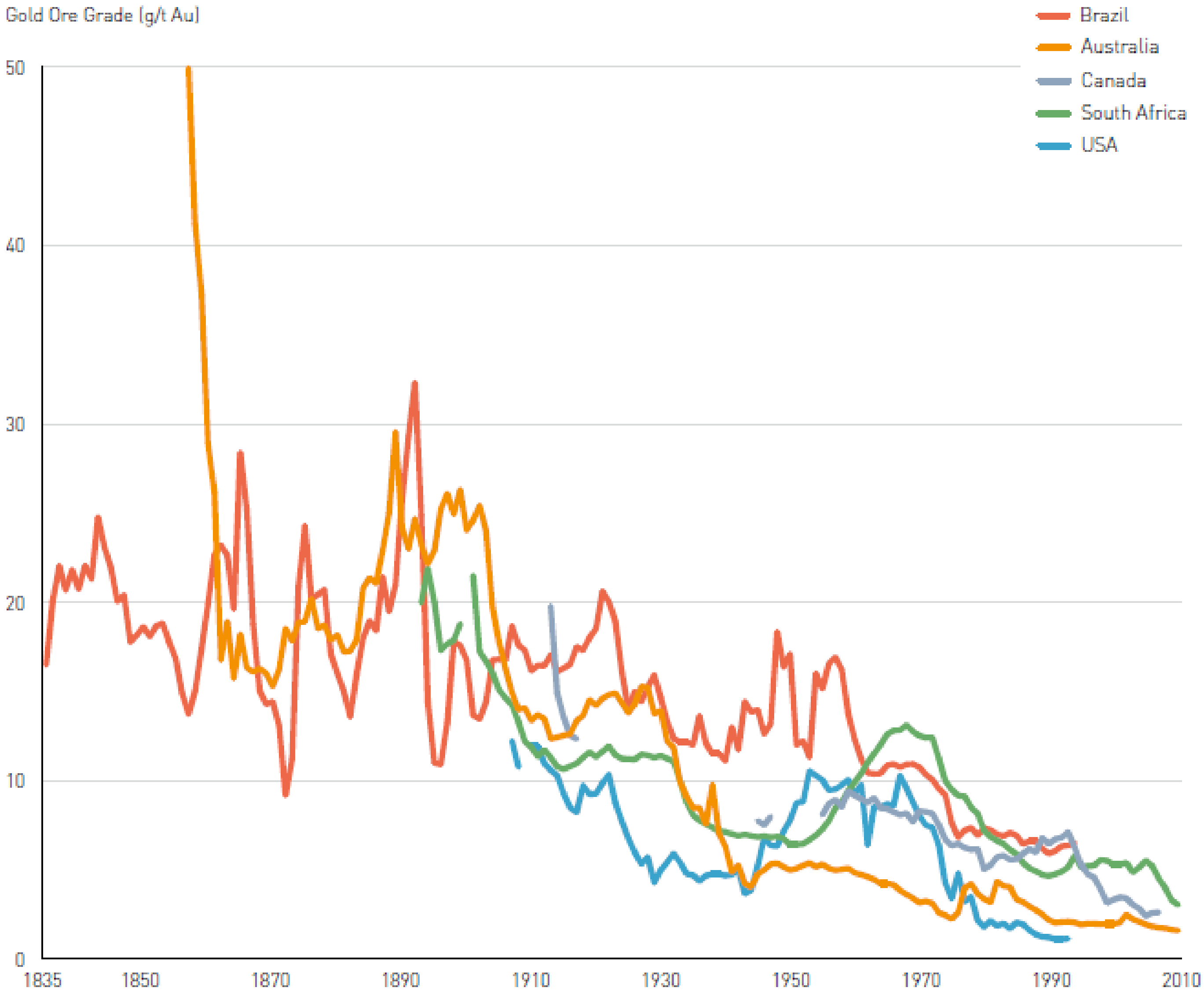
FPD (Fluid and Process Dynamics)
Research Group Leader
Advanced High Temp Refining and Impurities Removal, Processing of Secondary Resources, Metal Recycling

Extractive Metallurgy for Resource Efficiency and Circular Economy

- **Processing of Alternative Sources (Low Grade and Urban Ores)**
- **Metals Recovery/Recycling from Wastes**
- **Advanced Refining and Extraction Process**
- **Impurities Removal and Ultrapure Materials**
- **New Processes with Low Carbon Footprint**



Declining Metal Ore Grade Worldwide



UNEP. Recycling Rates of Metals – A status report, A report of the Working Group on the Global Metal Flows to the International Resource Panel, T.E. Graedel, et al. (2011)

Resource Efficiency and Circular Economy Context

Lowering of the grade of ores around the world

Availability of alternative resources for metals

- Low grade/weathered ores
- Urban ores
  - Industrial Wastes
  - Consumer/household Wastes
  - Construction Wastes
  - End of Life Products
  - **Electronic wastes**

Electronic wastes

- 40 million tonnes are generated annually (global)
- Great challenges and also opportunities
- <u>Contain:</u> Precious, Platinum Group, Base, Hazardous, and Rare Metals

Alternative Metal Ore Resources

10-15 kg

=

Containing 2g Au

=

500 kg to 1,000 kg

1,000 kg

=

200g (Au)

3 kg (Ag)

100 kg (Cu)

100 g (Pd)

What is E-Waste

Weight versus value distribution in E-Waste

Weights %	**Fe (wt %)**	**Al (wt %)**	**Cu (wt %)**	**Plastics (wt %)**	**Ag (ppm)**	**Au (ppm)**	**Pd (ppm)**
TV-board	28%	10%	10%	28%	280	20	10
PC-board	7%	5%	20%	23%	1000	250	110
Mobile phone	5%	1%	13%	56%	1380	350	210
Portable audio	23%	1%	21%	47%	150	10	4
DVD-player	62%	2%	5%	24%	115	15	4
Calculator	4%	5%	3%	61%	260	50	5
Value-share	Fe	Al	Cu	Sum Precious Metals	Ag	Au	Pd
TV-board	4%	11%	42%	43%	8%	27%	8%
PC-board	0%	1%	14%	85%	5%	65%	15%
Mobile phone	0%	0%	7%	93%	5%	67%	21%
Portable audio	3%	1%	77%	19%	4%	13%	2%
DVD-player	13%	4%	36%	47%	5%	37%	5%
Calculator	0%	5%	11%	84%	7%	73%	4%

Characteristics of E-Waste

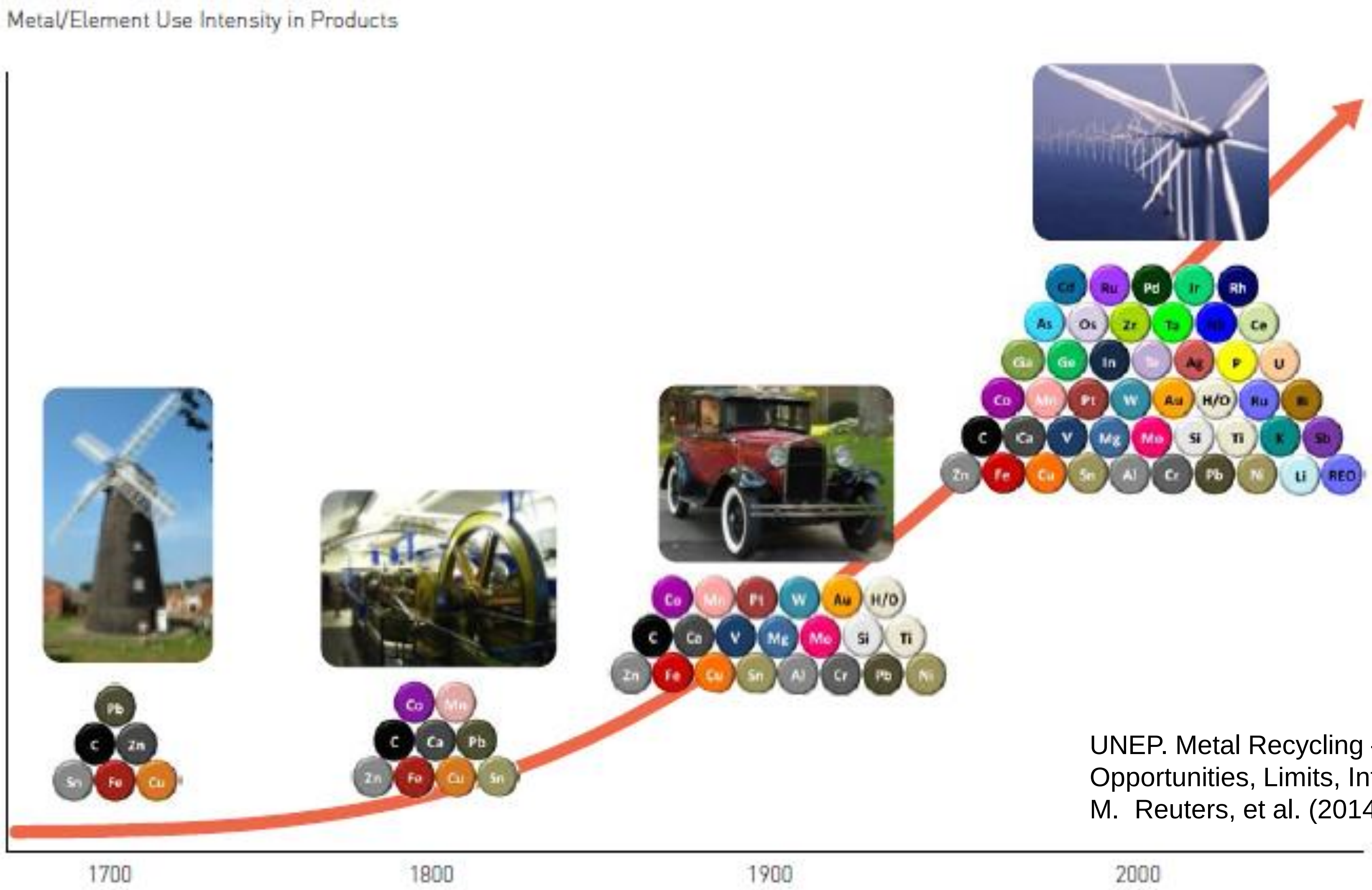
Complex microstructures

- **Contain remarkably different components**, e.g. plastics (hydrocarbons), glass (oxides), metals (ferrous and non-ferrous), and other components

Complex compositions

- The metals of interests are usually in **minor proportion (very low concentration)**
- They contain **large number of elements** (including valuable and hazardous substances), e.g. more than 40 metals on a cell phone
- Varies for different locations, products, and **time**

Increased Materials Complexity



UNEP. Metal Recycling – Opportunities, Limits, Infrastructure, M. Reuters, et al. (2014)

Technical Challenges

Fundamental knowledge

- A limited fundamental knowledge about this “new“ complex materials and how to effectively process them
    - **Thermodynamics, Kinetics, Separation, Refining, Extraction, and Materials etc**

Processing Technologies and Routes

- Extensive pre-processing and main extraction processes → longer overall process chains
- Development of new or modification of existing technologies and processes that is sustainable (economically and environmentally acceptable)
    - Systematic analyses of modified or new technologies and process routes, in terms of **techno-economic**, impact to environment (e.g. **life cycle assessment**), scale up from laboratory to full size plant, and feasibility, need to be considered

Non-Technical Challenges

Overall economic of the process

- This often becomes the **main driving force**
- New and **innovative business models** may also need to be developed to shift towards more economical process

Infrastructure and logistics

- Facilities for **pre-processing**, in addition to the main extraction processes facilities
- A good **collection system**, e.g. the network of collection, transportation of the resources and associated costs
- Consideration of the **size of the facilities**, from a small scale city-based to a large scale integrated smelting-recycling plants

Non-Technical Challenges

Government systems

- Governmental **policies** and **legislation** to promote and drive the market for processing towards the alternative resources
- Provide a **framework** for the development of innovative business models
- Government **incentives**

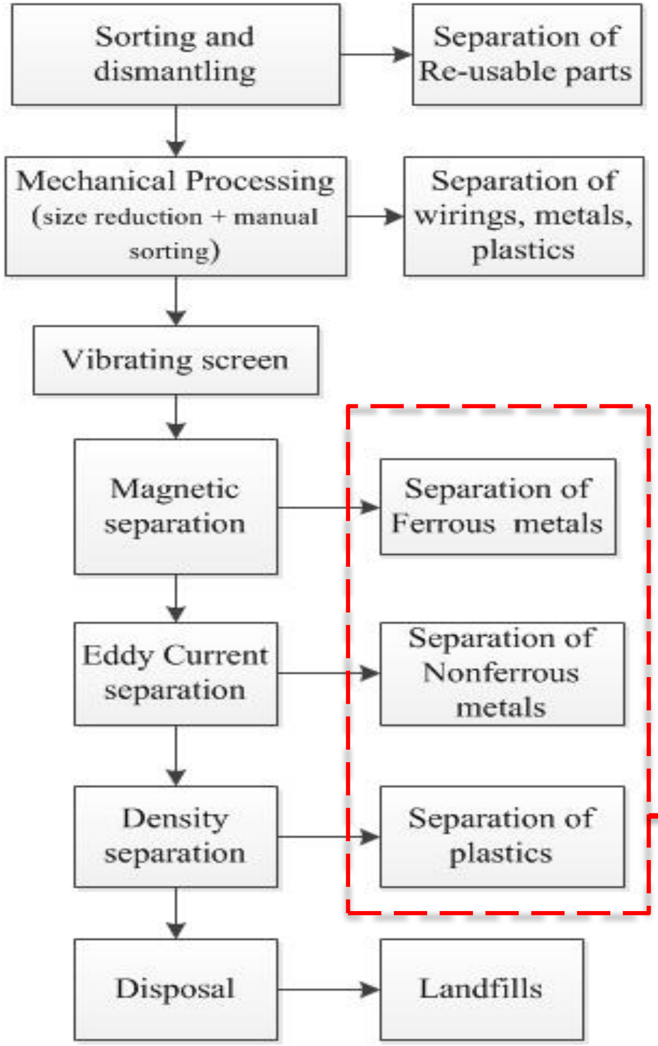
Social/socioeconomic challenges

- **Education** and **information** flow in the society about recycling and underlying wealth associated with the above ground “waste”
- Different **paradigms** and **cultures** within the society that can act as a barrier

General Steps in Processing of E-Waste

- **Collection**
  - Government policies
  - Public awareness
  - Easy access to collection facilities
- **Pre-processing**
  - Using similar method used in physical processing of ores
  - Sorting and dismantling (manual vs automatic)
  - Materials liberation (housing, wiring boards, drives)
  - Mechanical processing (shredder, hammer mills)
  - Separation of metals and non-metals (screening, magnetic, eddy current, density separation)
- **End-processing**
  - Further processing of non-metal and metal fractions
  - Metallurgical processes to recover metals

Pre-Processing of E-Waste



Sorting and dismantling → Separation of Re-usable parts

Mechanical Processing (size reduction + manual sorting) → Separation of wirings, metals, plastics

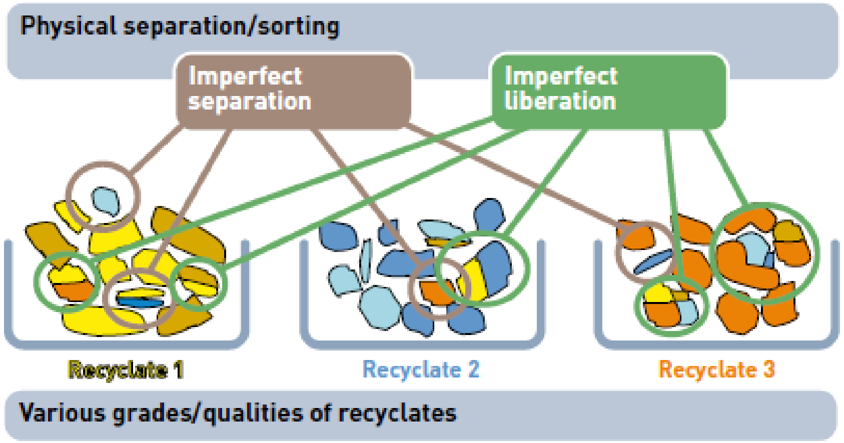
Vibrating screen

Magnetic separation → Separation of Ferrous metals

Eddy Current separation → Separation of Nonferrous metals

Density separation → Separation of plastics

Disposal → Landfills



Go to End-processing

The pre-processing of e-waste to separate metal and non-metal fractions

Particle size vs specific energy of treatment of PCB

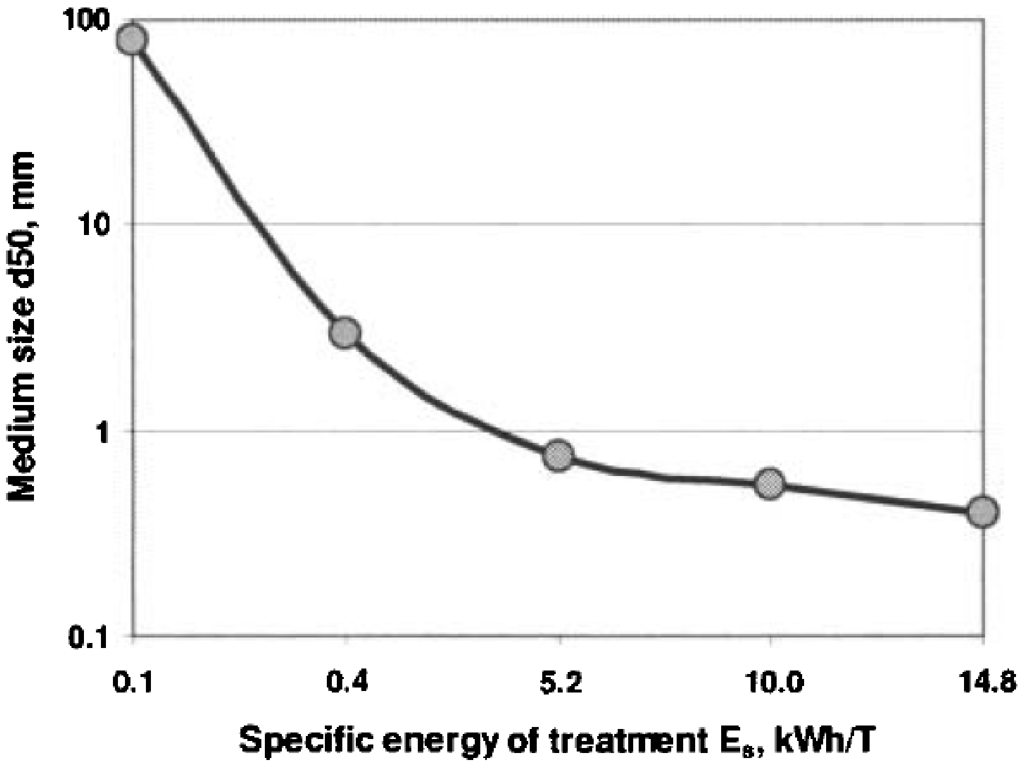
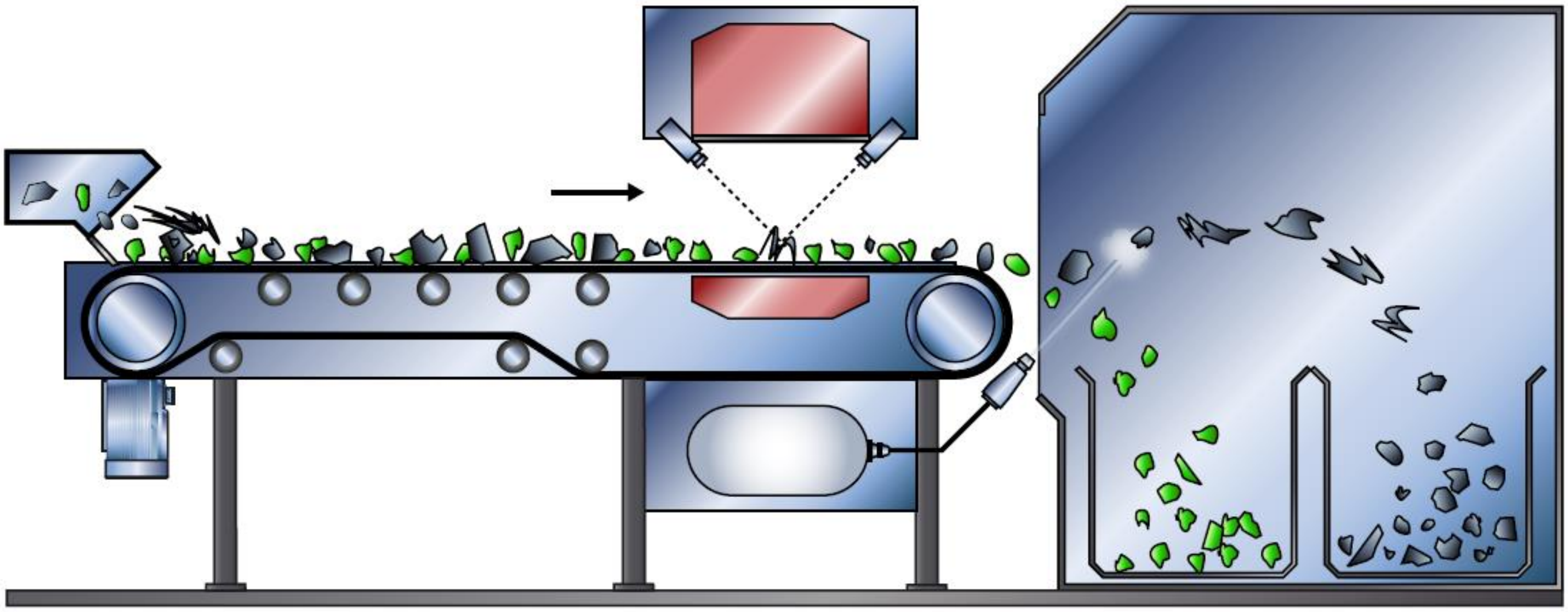


Fig. 2. Dependence of the particles medium size of PCBs on the specific energy of treatment

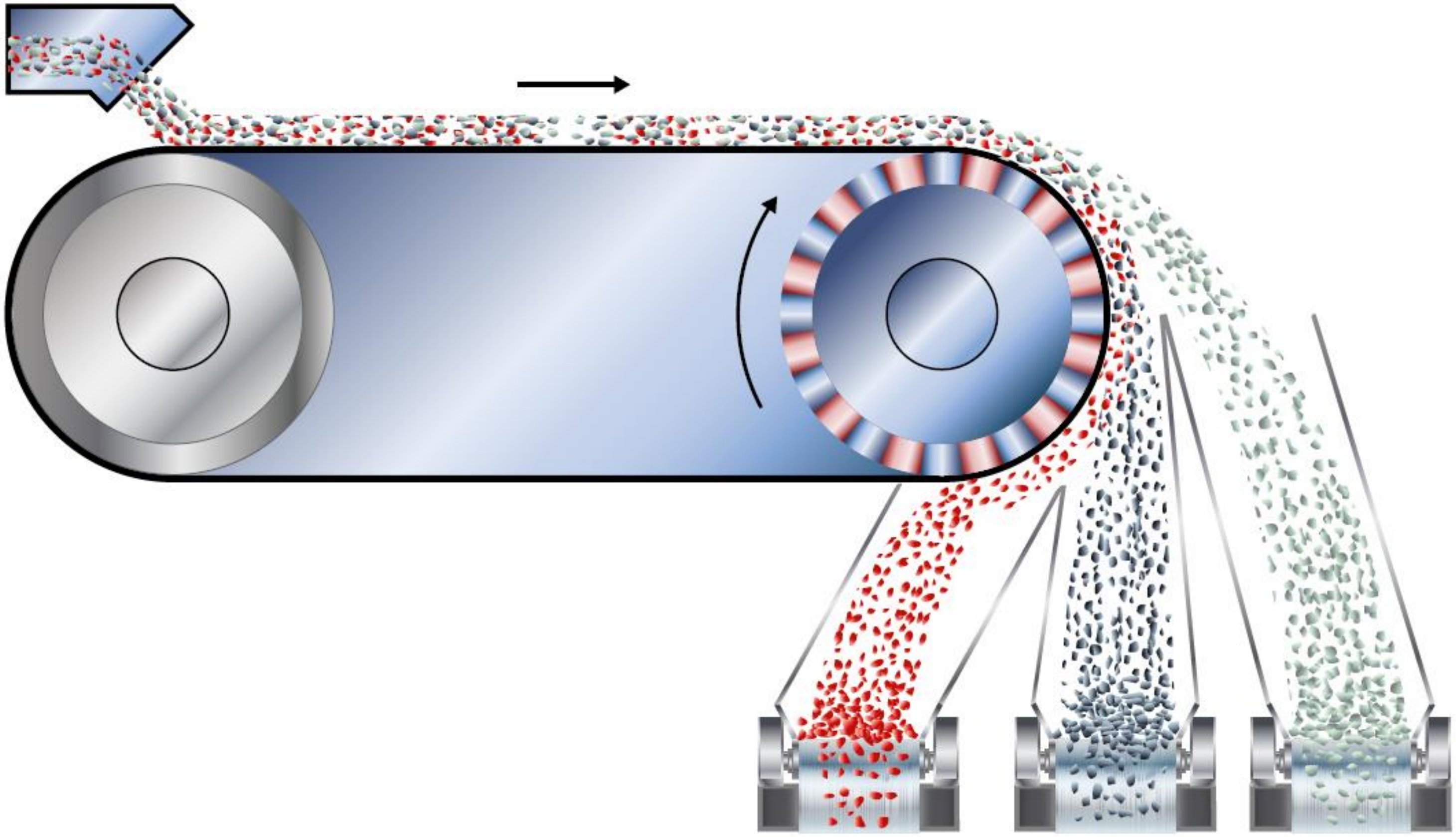
Laurmaa et al. TMS 2011

Sensor-based sorter



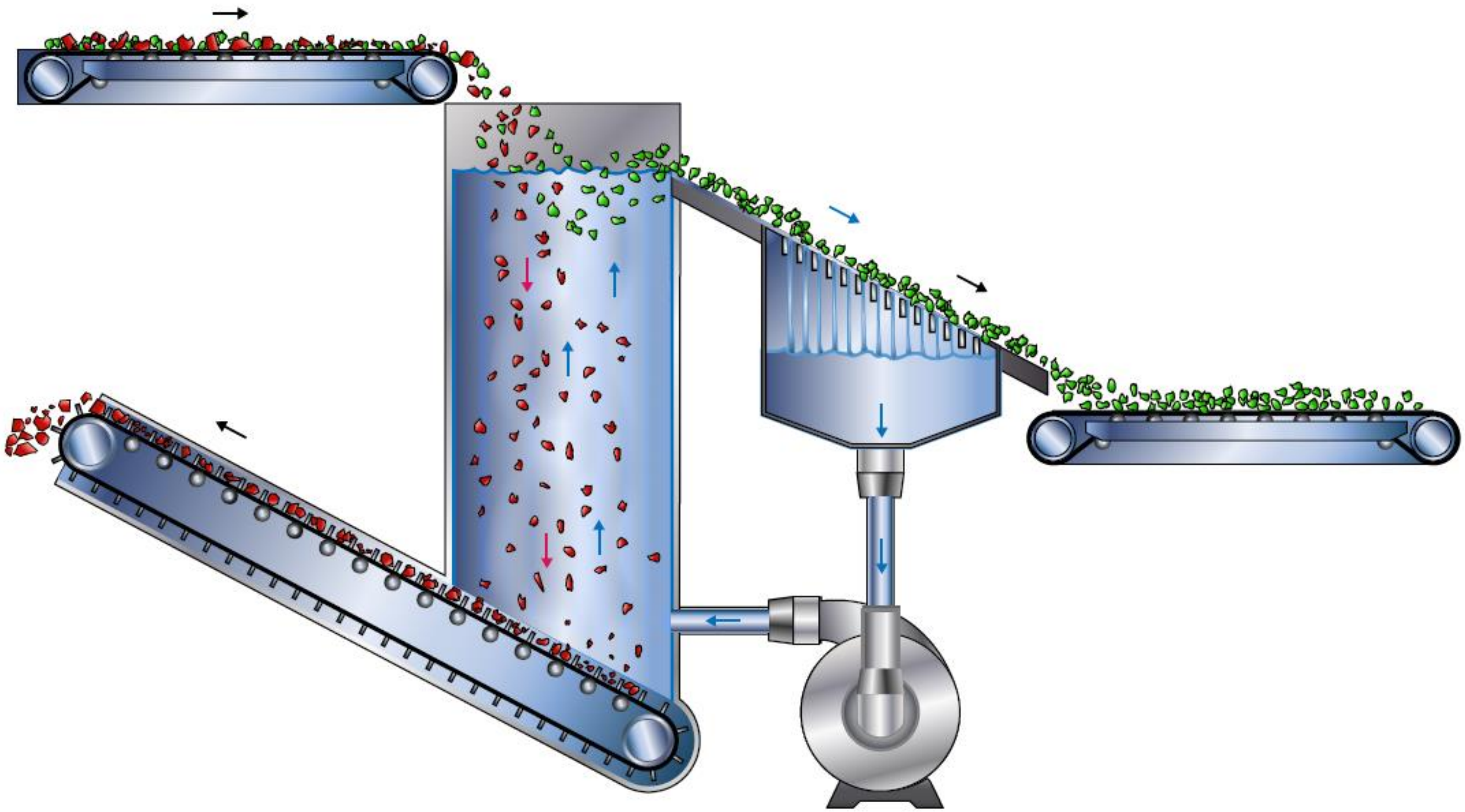
UNEP. Metal Recycling – Opportunities, Limits, Infrastructure, M. Reuters, et al. (2014)

Eddy Current separator



UNEP. Metal Recycling –
Opportunities, Limits, Infrastructure,
M. Reuters, et al. (2014)

Rising-Current separator



UNEP. Metal Recycling – Opportunities, Limits, Infrastructure, M. Reuters, et al. (2014)

Metallurgical Processes to Recover Metals from E-Waste

Hydrometallurgical routes

- Pre-processing and leaching using acid/caustic solutions
- Separation of precious metals from leachants using solvent extraction, adsorption, and ion exchange methods
- Metals extraction processes are similar to mineral processing

Pyrometallurgical routes

- Pre-processing is not necessary for small devices
- Direct feeding into furnace at high temperature
- Metal fraction end up in molten bath
- Plastics partially replace coke and act as reducing agent and fuel
- Oxides end up in slag phase

Metallurgical Processes to Recover Metals from E-Waste

Hydrometallurgy Route

Investigators	Leaching agent	Process conditions	Recovered metals
Park and Fray [41]	Aqua regia	Ratio of metals to leachant = 1:20 g/ml	Au, Ag, Pd
Sheng and Estell [50]	HNO_3 (1st stage), Epoxy resin (2nd stage), Aqua regia (3rd stage)	Extraction was carried out in three stages (Self agitation)	Au
Quinet et al [51]	H_2SO_4, Chloride, thiourea, cyanide leaching	Leaching & metals recovery by cementation, precipitation, ion exchange and carbon adsorption	Au, Ag, Pd, Cu
Chielewski et al [52]	HNO_3 Aqua regia	Roasting of E-waste in the presence of carbon Leaching with HNO_3 and aqua regia Solvent extraction with diethyle malonate	Au
Zhou et al [53]	HCl, H_2SO_4 $NaClO_3$	Combustion of E-waste at 400-500^{o}C followed by leaching.	Ag, Au, Pd
Kogan [54]	HCl, $MgCl_2$, H_2SO_4 H_2O_2	Dissolution of E-waste in different solvents and conditions Recovery of metals in stages	Al, Sn, Pb and Zn (1st stage), Cu and Ni (2nd stage), Au, Ag, Pd and Pt (last stage)
Veit et al [11]	Aqua regia H_2SO_4	Mechanical processing and then dissolution of e-waste in different solvents	Cu
Mecucci and Scott [55]	HNO_3	Electrochemical deposition of Cu at cathode from solution	Pb, Cu

Table 7: Summary of hydrometallurgical recovery of precious metals from e-waste (Khaliq et al 2014)

Limitations of Hydrometallurgy Route

- In general slow and time consuming → impact on recycling economy
- Longer mechanical pre-processing of e-waste to reduce size for efficient dissolution. 20% precious metal could be lost during liberation process
- Problems associated with leachant
    - cyanide – hazardous, environmentally unfriendly
    - halide – corrosive and oxidizing
    - thiourea – high cost and consumption
    - thiosulfate – high consumption
- There are possibilities of precious metals loss during dissolution and subsequent steps, therefore the overall recovery of metals will be affected

Metallurgical Processes to Recover Metals from E-Waste

Pyrometallurgy Route

- The use of high temperature to process E-waste
- Smelting in furnaces, incineration, combustion and pyrolysis
- Liberation, separation/upgrading and purification are carried out by exploiting metals chemical and metallurgical properties, e.g. precious metals are segregated into **copper** or **lead** → make a precious metals “concentrate” using metal carrier
- Currently, copper and lead smelters work as e-waste recyclers for the recovery of Pb, Cu and precious metals
- Understanding of thermodynamics and process metallurgy are required to optimize process

Copper Smelting Route

Primary Copper Production Route

- Sulphide ores processed to produce copper matte (40%Cu) then to blister copper (98.5%). Finally, blister copper is refined by fire refining and electrorefining to produce pure copper

Secondary Copper Production Route

- e.g. the black copper route
- consists of reduction and oxidation cycles
- followed by refining in anode furnace and electrorefining to produce pure copper
- The precious metals go with the copper, and segregated into anode slime after the electrorefining and further processes for recovery

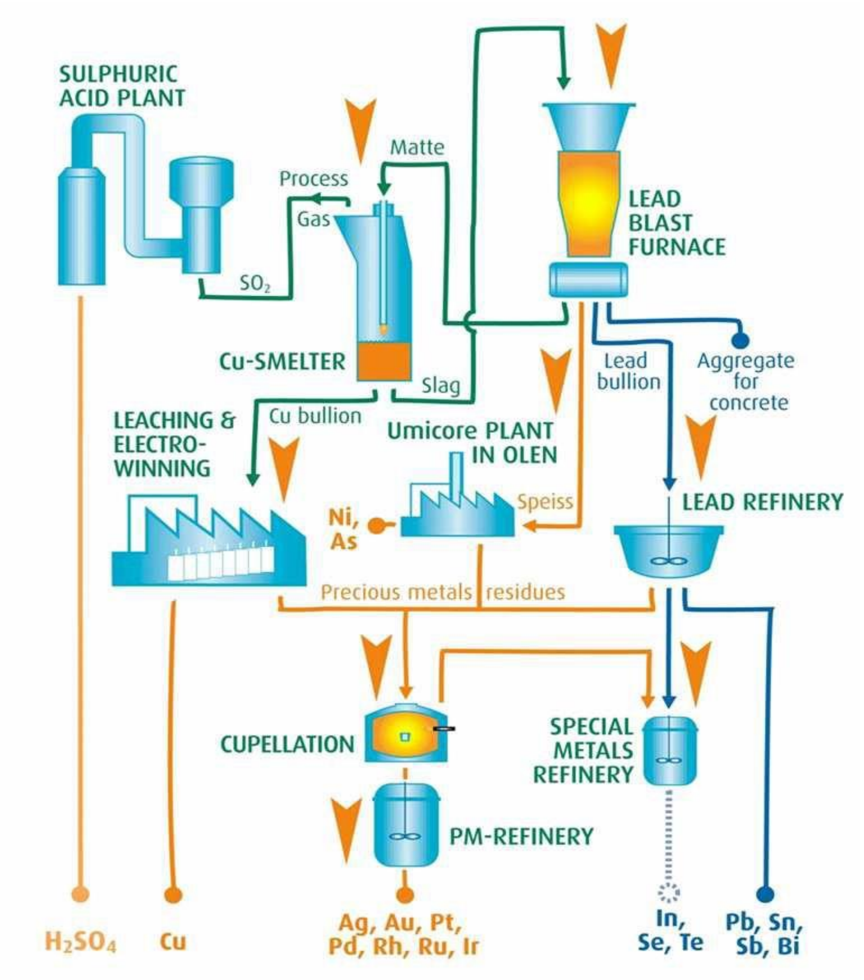
Industrial Processes for Recovery of Metals from E-Waste

Copper Smelting Route

- Umicore integrate smelting and refining facility, Belgium
- Noranda process in Quebec, Canada
- Rönnskär smelters in Sweden
- Kosaka recycling plant in Japan
- Kayser recycling system KRS in Austria and Germany
- Metallo-Chimique N.V plants in Belgium and Spain

Integrated Smelting and Refining

A flowsheet for Umicore's integrated metals smelter and refinery, Hageluken (2006)



Aerial view of Umicore plant at Hoboken/Antwerp, Hageluken and Corti (2010)

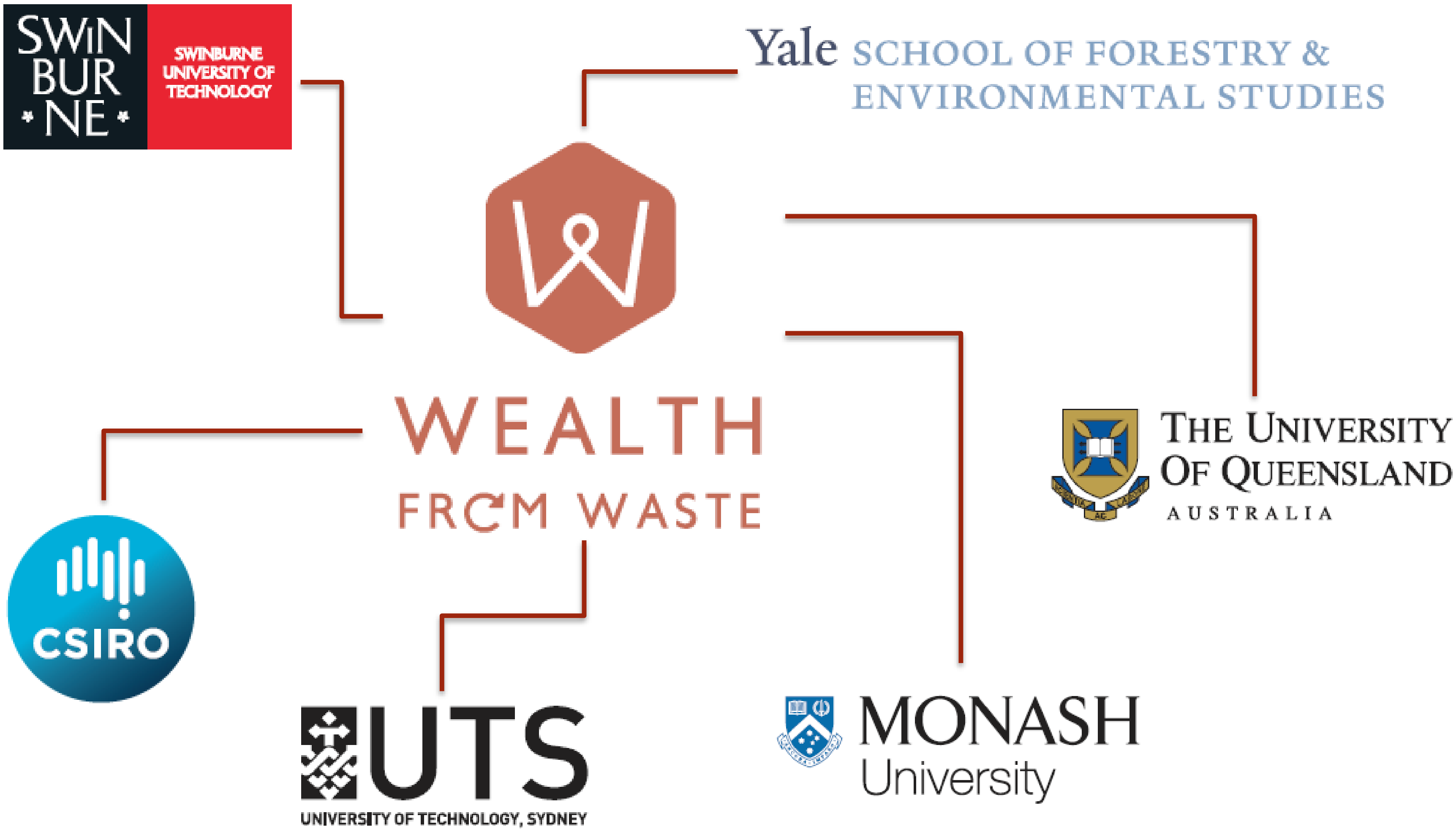
Integrated Smelting and Refining

Summary of selected pyrometallurgical methods for recovery of metals from e-waste

Industrial processes	Metals recovered	Main process features
Umicore's process [20, 63, 64]	Au, Ag, Pd, Pt, Se, Ir, Ru, Rh, Cu, Ni, Pb, In, Bi, Sn, As, Sb	IsaSmelt smelting, copper leaching & electrowinning and precious metals refinery
Outotec TSL [68]	Zn, Cu, Au, Ag, In, Pb, Cd, Ge	Top submerged lanced furnace (Ausmelt TSL), Smelting of e-waste in copper/lead/zinc processes
Rönnskär smelters [66, 69]	Cu, Ag, Au, Pd, Ni, Se, Zn, Pb	Smelting in Kaldo reactor, upgrading in copper and followed by refining, high precious metals recovery
Noranda process [67]	Cu, Au, Ag, Pt, Pd, Se, Te, Ni	Smelting of e-waste and Cu concentrate. Upgrading in converter and anode furnaces. Electrorefining for metal recovery
Rönnskär smelters [66, 70]	Cu and precious metals	PC scrap feeding to Zn fuming process, Plastics is used as reducing agent, Precious metals are segregated in Cu and are recovered at later stage
Umicore's trials [71]	Au, Ag, Pd, Pt, Se, Ir, Ru, Rh, Cu, Ni, Pb, In, Bi, Sn, As, Sb	Plastics from e-waste is tested at energy and reducing agent during smelting
Dowa mining Kosaka Japan [72]	Cu, Au, Ag	E-waste smelting in copper flash converter
LS-Nikko,s recycling facility, Korea [73]	Au, Ag & PGMs metals	Recycling in TSL smelting followed by electrolytic refining
Day's patent [74]	Precious metals, Pt and Pd	Smelting in plasma arc furnace at 1400ºC. Precious metals collected in base metal. Ceramic residue went in the slag phase. Ag and Cu used to collect metals during process
Aleksandrovich patent [75]	PGMs and gold	Scrap combustion in a base metal using carbon as reducing agent, Solidification and separation of solidified product are carried out by formed phase boundaries
Aurubis recycling Germany [76]	Cu, Pb, Zn, Sn and PMs	Smelting of Cu and e-waste in TSL reactor, black copper processing and finally electrorefining

Research Cluster Wealth from Waste in Australia

Research Cluster Wealth from Waste



Approach

1. **Evaluation of the various existing processes, technologies, and process routes [1,2]**

2. **Select a potential process route to be further investigated / studied**
    - Technologically feasible
    - High potential to deliver a bigger impact
    - Deliver value, flexible process, economically viable, environmentally acceptable

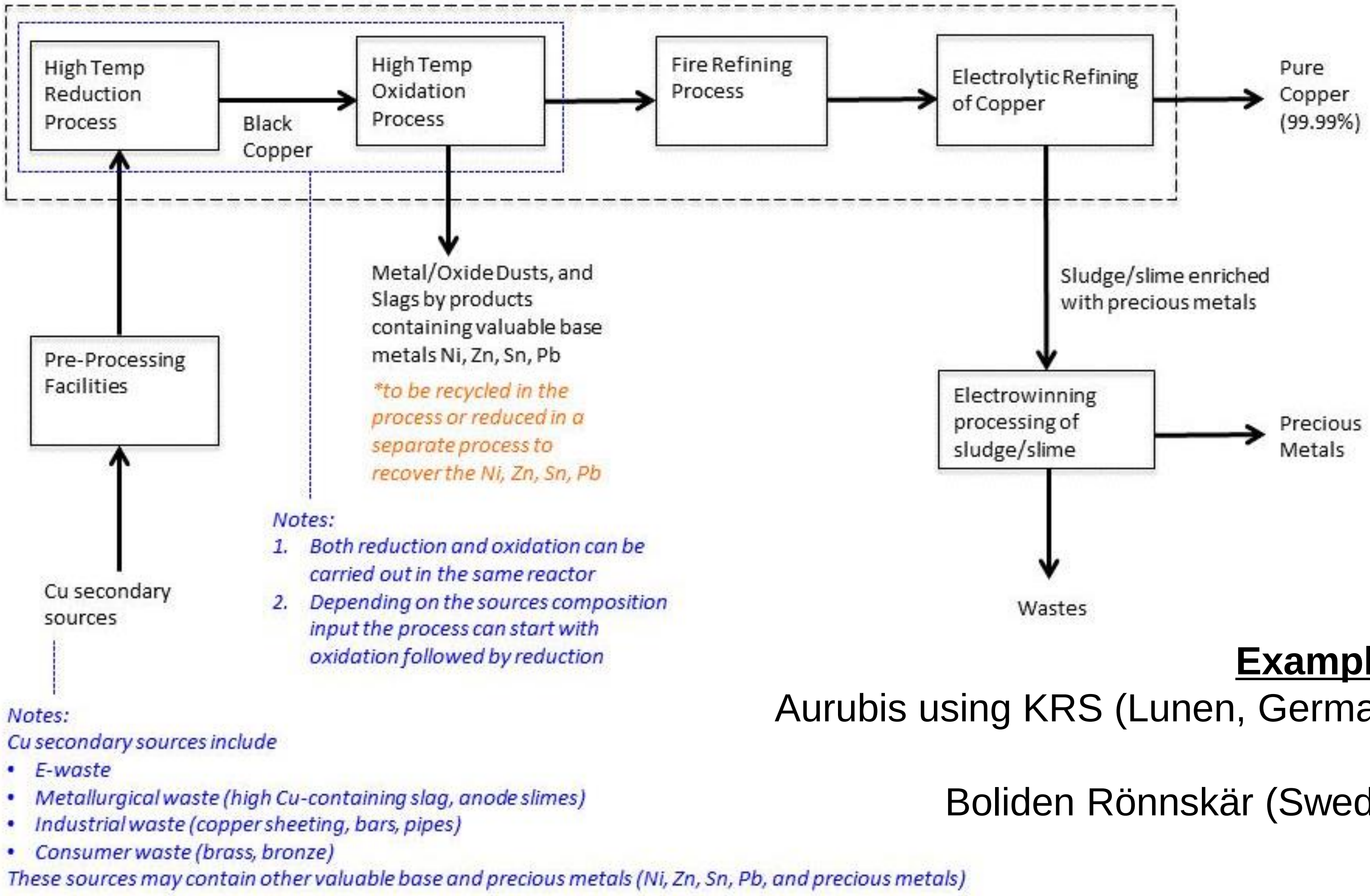
3. **Carry out combined thermodynamics, process flowsheeting, technoeconomic and life cycle assessment modelling studies**

1. A. Khaliq, M.A. Rhamdhani, et al, "Metal Extraction Processes for Electronic Waste and Existing Industrial Routes: A Review and Australian Perspective", *Resources,* 3(1), 2014, 152-179 **(+ 53,000 downloaded)**

2. M. Firdaus, M.A. Rhamdhani, et al, “Review of High Temperature Recovery of Rare Earth (Nd/Dy) from Magnet Waste”, *Journal of Sustainable Metallurgy,* 2(4), Dec 2016, 276-95.

Selected Process Route

Black Copper Smelting Route



High Temp Reduction Process

Black Copper

High Temp Oxidation Process

Fire Refining Process

Electrolytic Refining of Copper

Pure Copper (99.99%)

Metal/Oxide Dusts, and Slags by products containing valuable base metals Ni, Zn, Sn, Pb

**to be recycled in the process or reduced in a separate process to recover the Ni, Zn, Sn, Pb*

Sludge/slime enriched with precious metals

Electrowinning processing of sludge/slime

Precious Metals

Wastes

Pre-Processing Facilities

Cu secondary sources

Notes:

1. *Both reduction and oxidation can be carried out in the same reactor*
2. *Depending on the sources composition input the process can start with oxidation followed by reduction*

Notes:

Cu secondary sources include

- *E-waste*
- *Metallurgical waste (high Cu-containing slag, anode slimes)*
- *Industrial waste (copper sheeting, bars, pipes)*
- *Consumer waste (brass, bronze)*

These sources may contain other valuable base and precious metals (Ni, Zn, Sn, Pb, and precious metals)

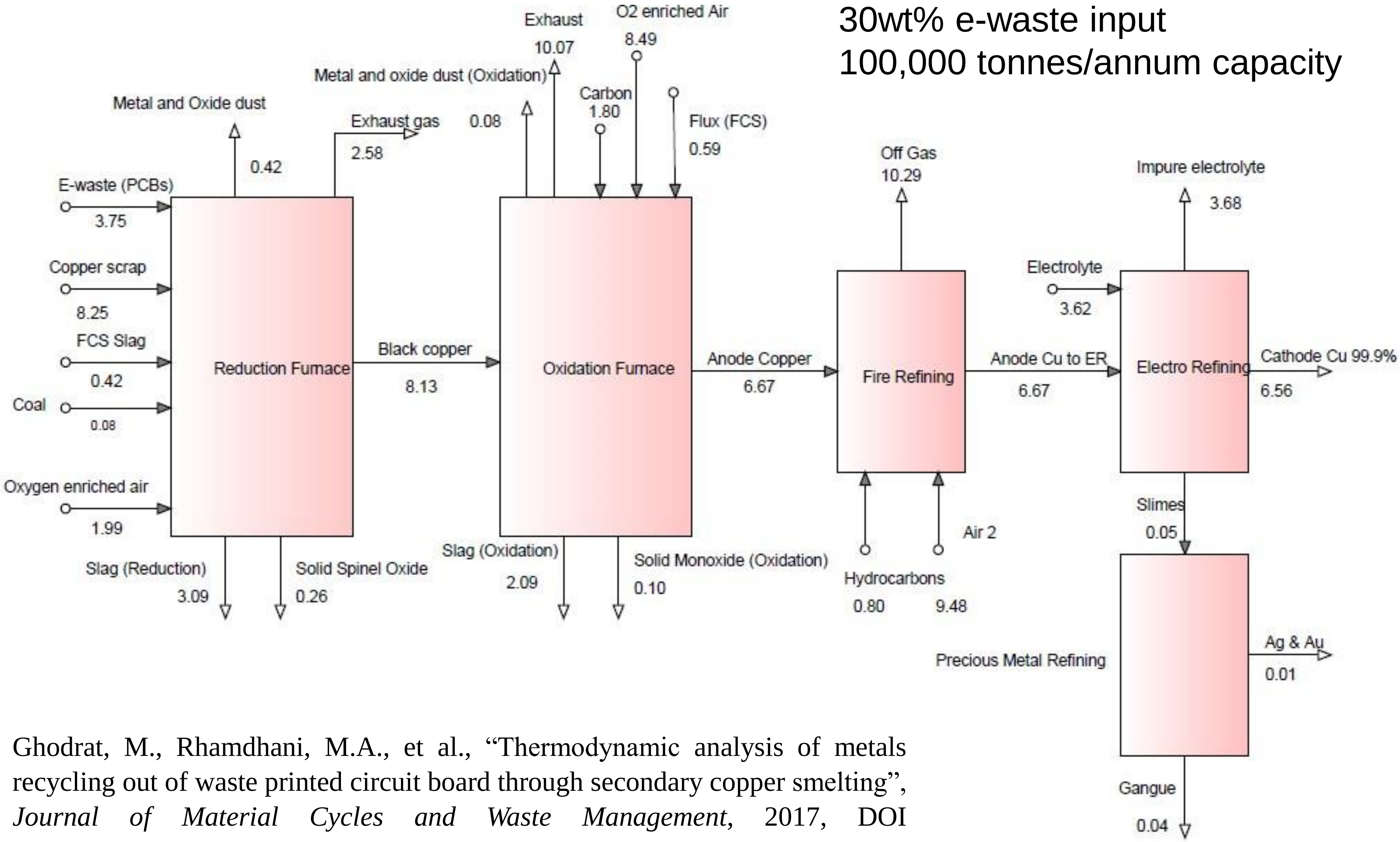
Examples:

Aurubis using KRS (Lunen, Germany)

Boliden Rönnskär (Sweden)

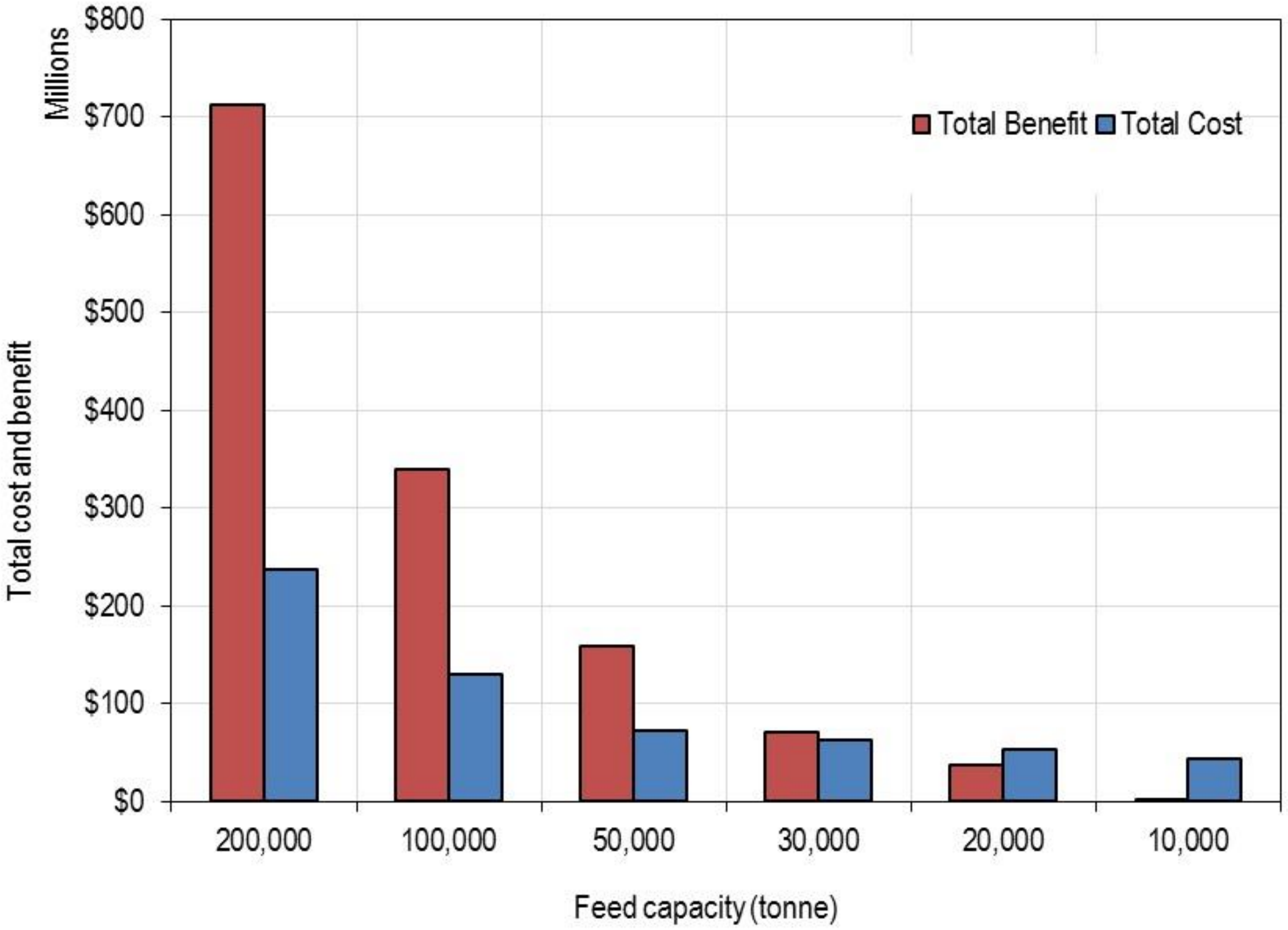
Process Flowsheet: Mass and Energy Balance

30wt% e-waste input
100,000 tonnes/annum capacity

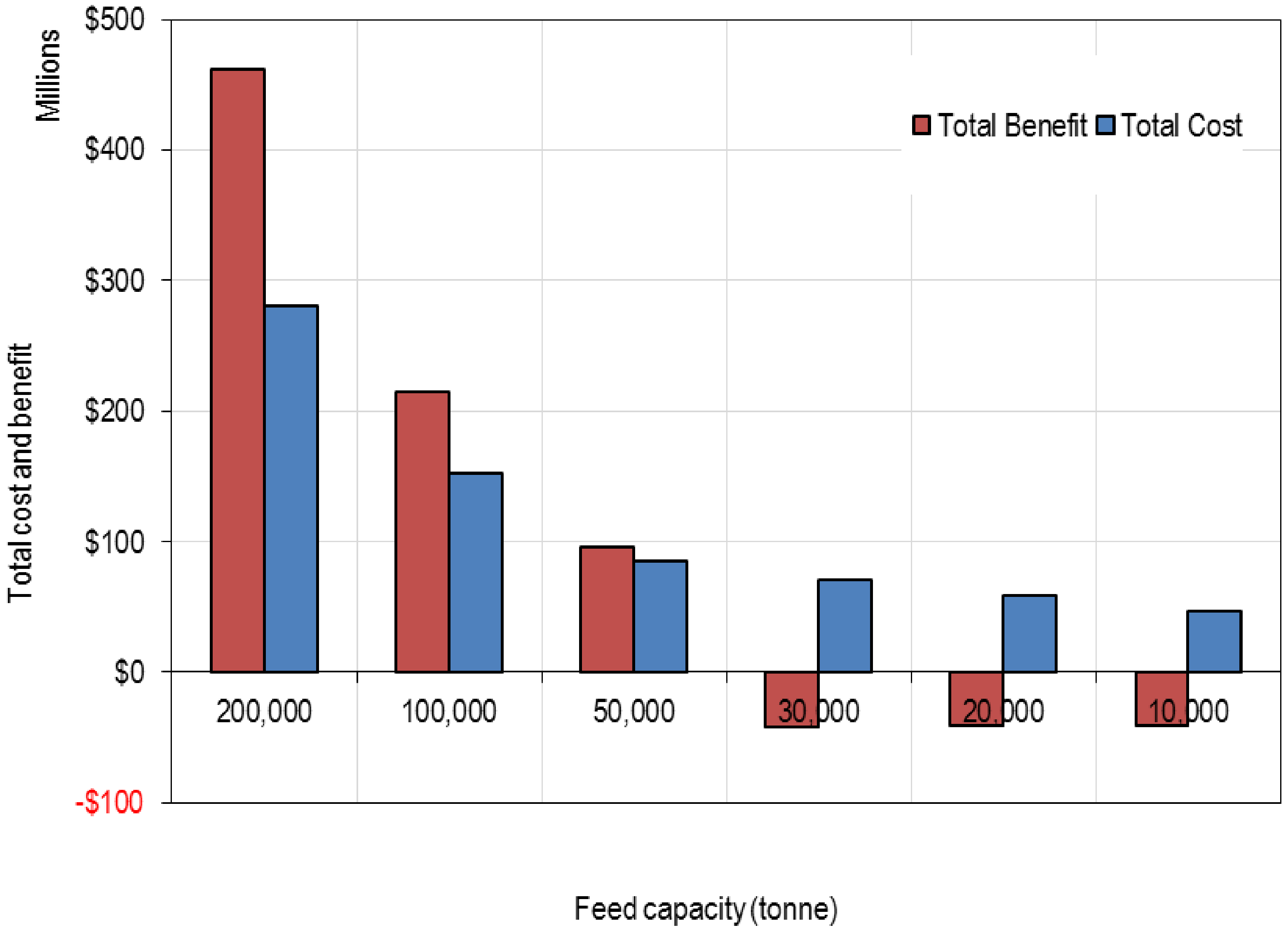


Ghodrat, M., Rhamdhani, M.A., et al., "Thermodynamic analysis of metals recycling out of waste printed circuit board through secondary copper smelting", *Journal of Material Cycles and Waste Management*, 2017, DOI 10.1007/s10163-017-0590-8.

Effect of Production Scale on the Economic



Effect of Transportation Cost



50wt% e-waste input

Challenges in Thermodynamic

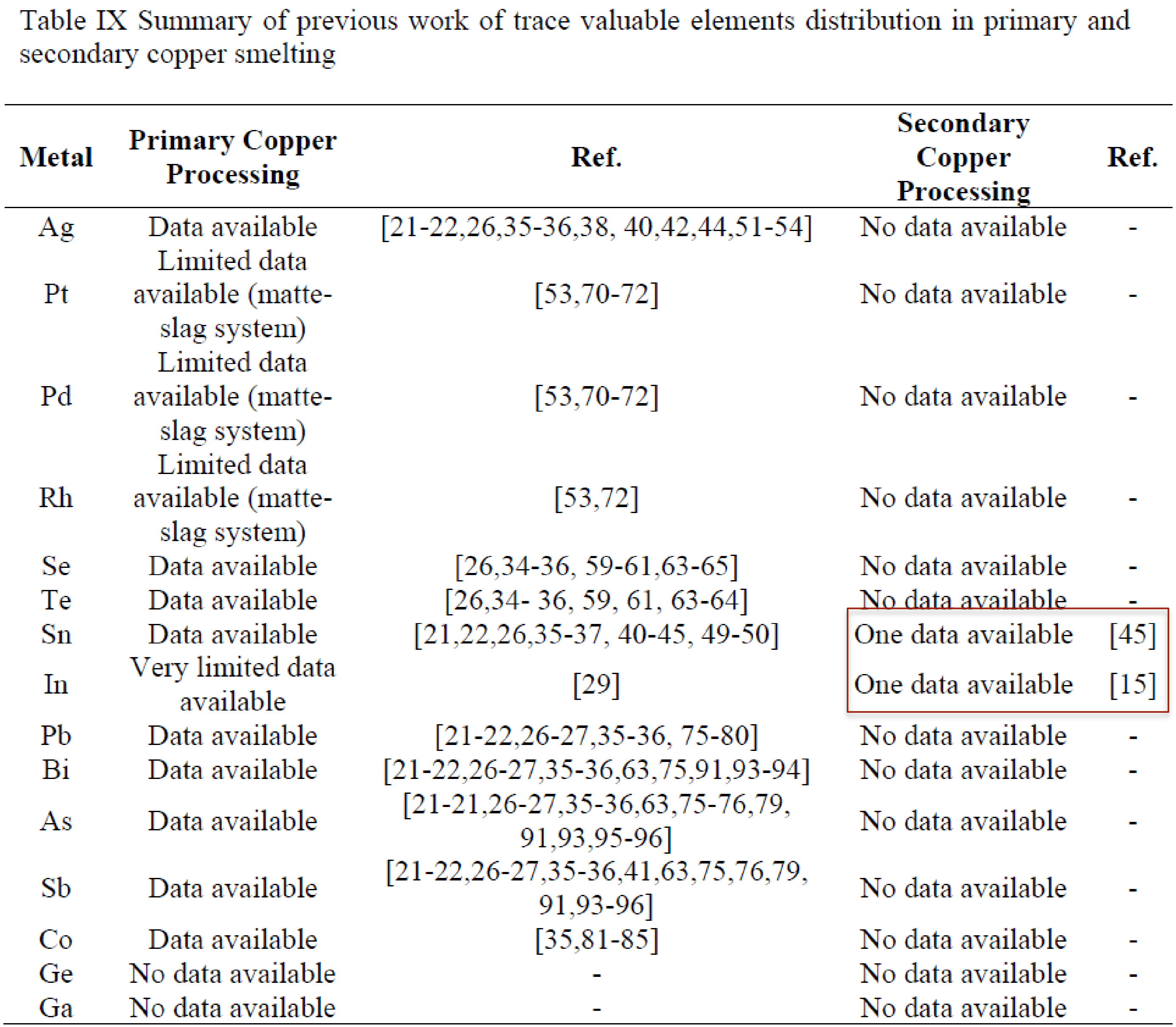


Table IX Summary of previous work of trace valuable elements distribution in primary and secondary copper smelting

Metal	Primary Copper Processing	Ref.	Secondary Copper Processing	Ref.
Ag	Data available	[21-22,26,35-36,38, 40,42,44,51-54]	No data available	-
Pt	Limited data available (matte-slag system)	[53,70-72]	No data available	-
Pd	Limited data available (matte-slag system)	[53,70-72]	No data available	-
Rh	Limited data available (matte-slag system)	[53,72]	No data available	-
Se	Data available	[26,34-36, 59-61,63-65]	No data available	-
Te	Data available	[26,34- 36, 59, 61, 63-64]	No data available	-
Sn	Data available	[21,22,26,35-37, 40-45, 49-50]	One data available	[45]
In	Very limited data available	[29]	One data available	[15]
Pb	Data available	[21-22,26-27,35-36, 75-80]	No data available	-
Bi	Data available	[21-22,26-27,35-36,63,75,91,93-94]	No data available	-
As	Data available	[21-21,26-27,35-36,63,75-76,79, 91,93,95-96]	No data available	-
Sb	Data available	[21-22,26-27,35-36,41,63,75,76,79, 91,93-96]	No data available	-
Co	Data available	[35,81-85]	No data available	-
Ge	No data available	-	No data available	-
Ga	No data available	-	No data available	-

M.A.H. Shuva, M.A. Rhamdhani, et al, “Thermodynamics data of valuable elements relevant to e-waste processing through primary and secondary copper production – a review”, *Journal of Cleaner Production*, 2016, Vol. 131, pp.795-809

Thermodynamic Behavior of Valuable Elements during Black Copper Smelting

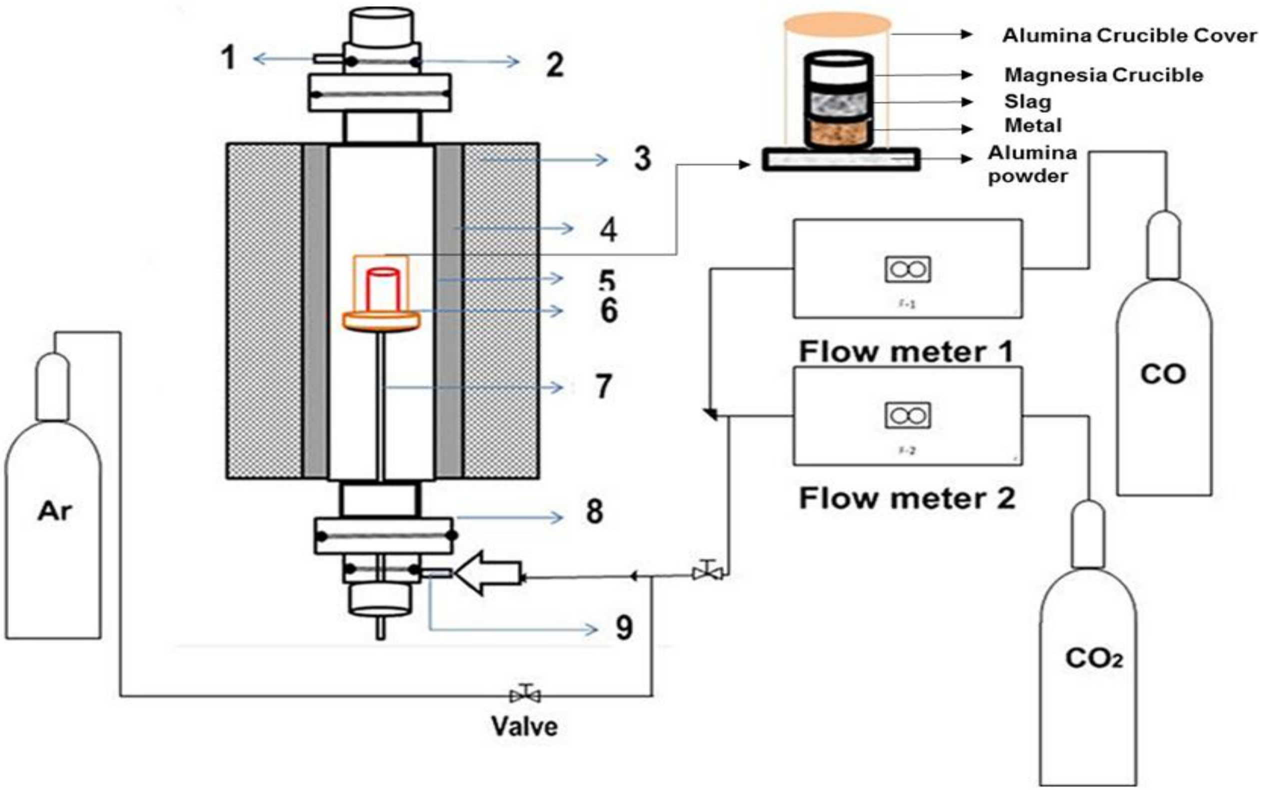


Fig. 6: A schematic of vertical tube furnace with experimental set up

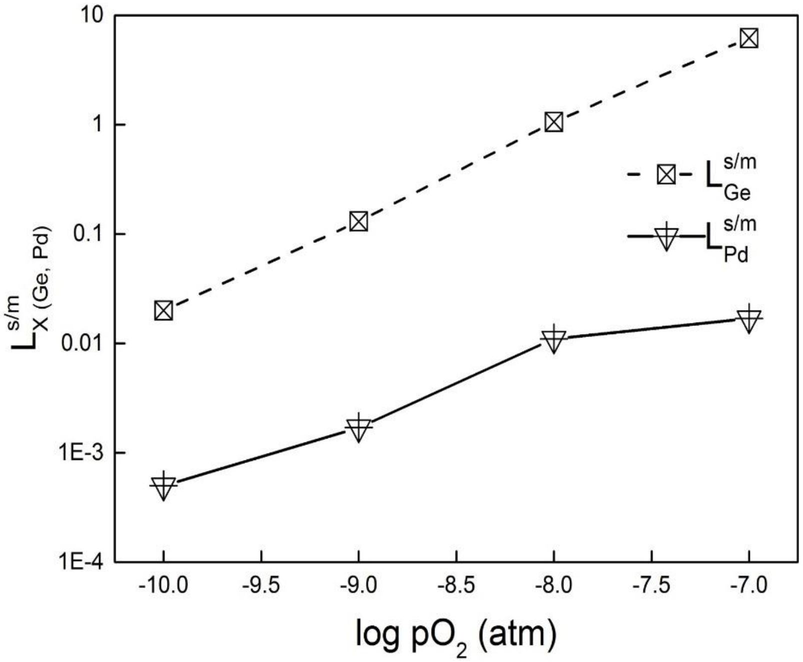
Legend : 1. Gas outlet, 2. Silicone O ring 3. $MoSi_2$ heating element 4. Alumina Tube 5. Mullite Tube 6. Magnesia Crucible 7. Alumina Pedestal 8. Water Cooled Flange 9. Gas Inlet

$T = 1200 – 1350^{o}C$
$pO_2 = 10^{-7} – 10^{-10}$ atm

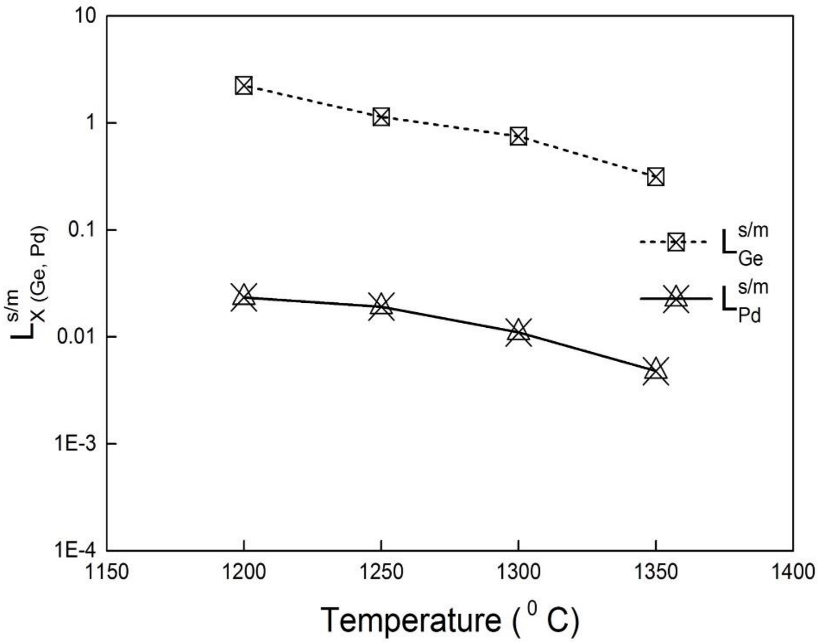
Slag:
FeO_x-CaO-SiO_2-MgO

Metal;
Cu/Ge, Cu/Pd, Cu/Ta

Effect of Oxygen Potential and Temperature



Distribution ratio in FeOx-SiO_2-CaO-MgO slag and metal as a function of oxygen partial pressure at 1573 K



Distribution ratio in FeOx-SiO_2-CaO-MgO slag and metal as a function of temperature

$$\mathrm{L}_{\mathrm{Ge}}^{s/m} = \frac{181}{75}\log p_{O_2} + \frac{61422}{\mathrm{T}} - \frac{365}{36}\ {Q^3}\!\Big/_{Q^2} - \frac{115}{8}$$

$$\mathrm{L}_{\mathrm{Pd}}^{\mathrm{S/m}} = \frac{74}{9999}\log p_{O_2} - \frac{724}{T} + \frac{8}{21}\ {Q^3}\!\Big/_{Q^2} + \frac{2}{5}$$

Shuva, M.A.H., Rhamdhani, M.A. et al., “Structural Analysis of Ge-containing Ferrous Calcium Silicate Magnesia Slag for Applications of Black Copper Smelting”, TMS 2018, Phoenix Arizona.

Distribution data for trace valuable metals at black copper smelting conditions

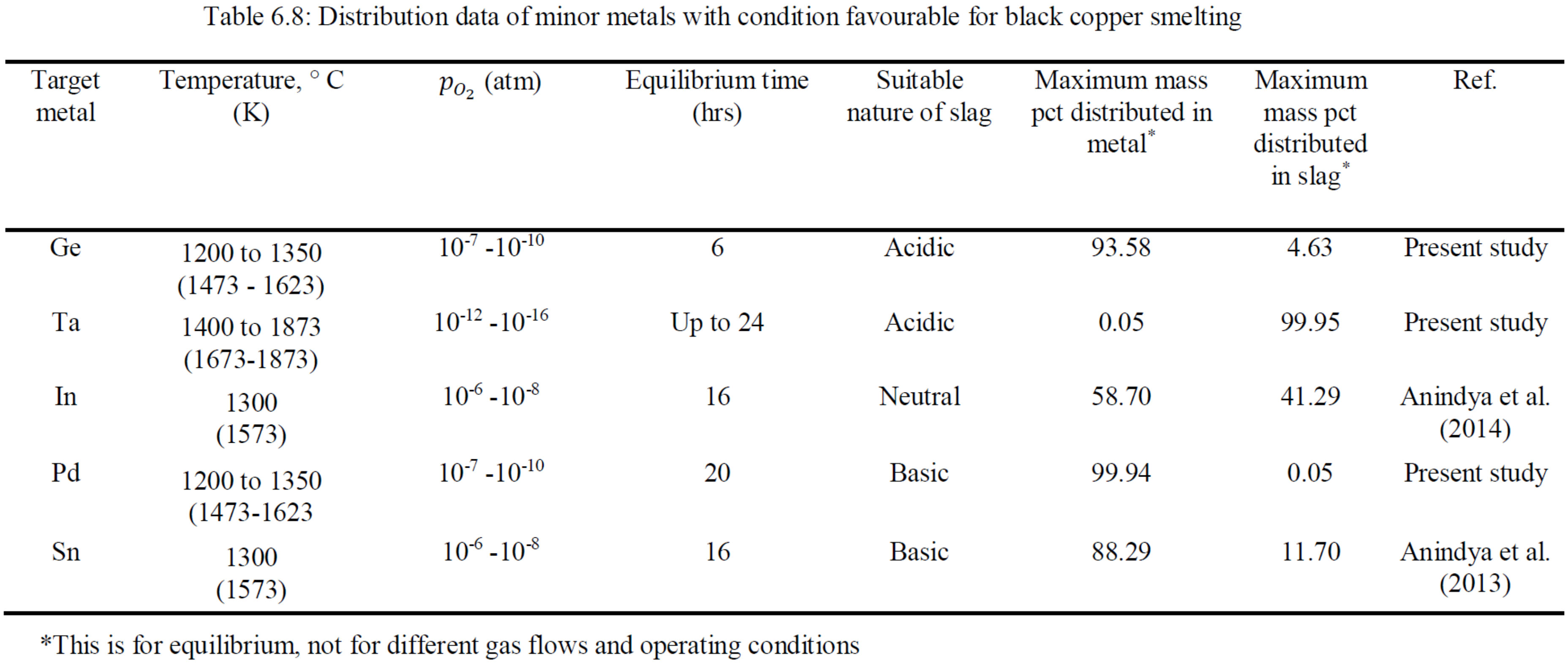


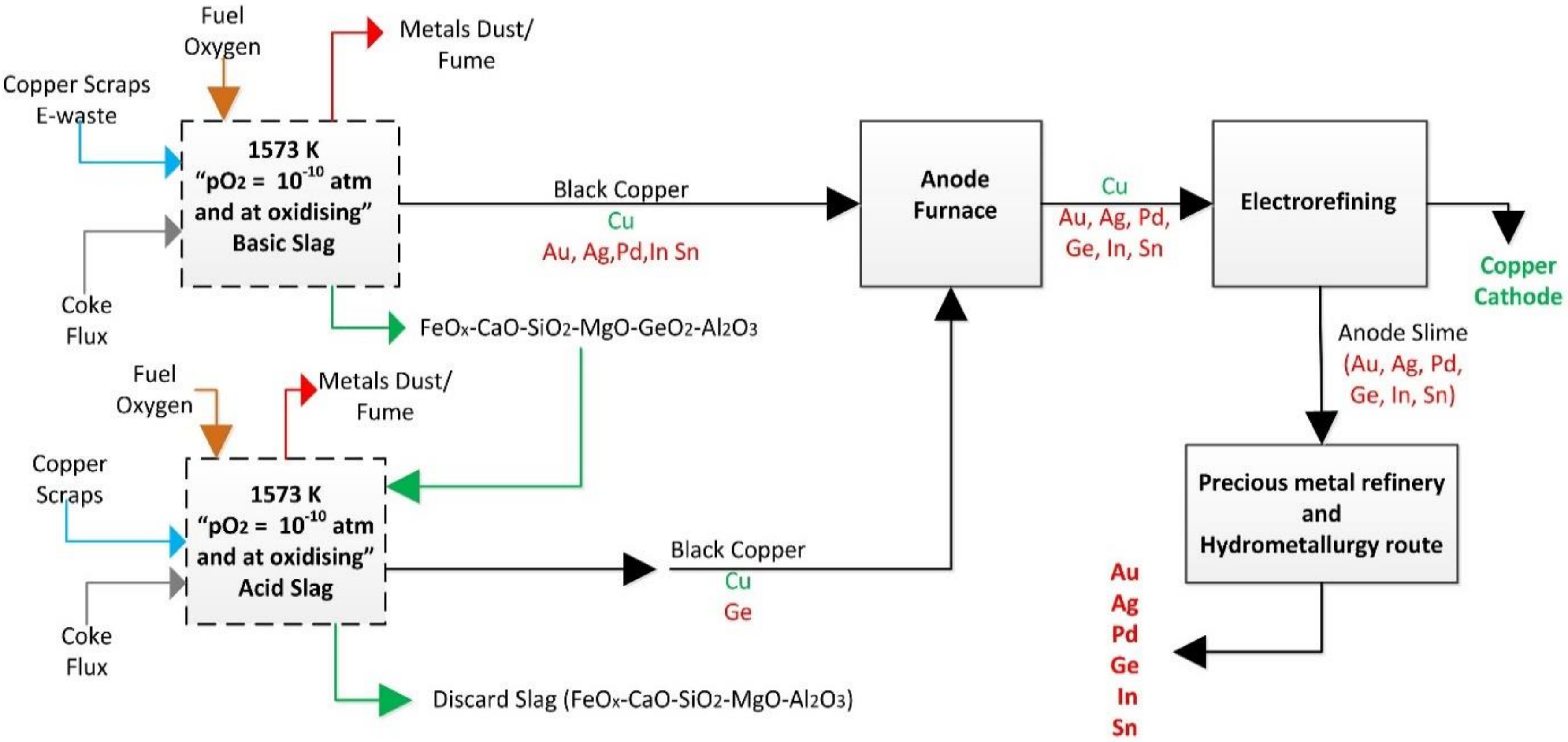
Table 6.8: Distribution data of minor metals with condition favourable for black copper smelting

Target metal	Temperature, ° C (K)	p_{O_2} (atm)	Equilibrium time (hrs)	Suitable nature of slag	Maximum mass pct distributed in metal*	Maximum mass pct distributed in slag*	Ref.
Ge	1200 to 1350 (1473 - 1623)	10^{-7} -10^{-10}	6	Acidic	93.58	4.63	Present study
Ta	1400 to 1873 (1673-1873)	10^{-12} -10^{-16}	Up to 24	Acidic	0.05	99.95	Present study
In	1300 (1573)	10^{-6} -10^{-8}	16	Neutral	58.70	41.29	Anindya et al. (2014)
Pd	1200 to 1350 (1473-1623	10^{-7} -10^{-10}	20	Basic	99.94	0.05	Present study
Sn	1300 (1573)	10^{-6} -10^{-8}	16	Basic	88.29	11.70	Anindya et al. (2013)

*This is for equilibrium, not for different gas flows and operating conditions

- Shuva, M.A.H., Rhamdhani, M.A., et al., "Thermodynamics of Palladium (Pd) and Tantalum (Ta) Relevant to Secondary Copper Smelting", *Metallurgical and Materials Transactions B*, Vol.48 (1), 2017, pp.317-27.
- Shuva, M.A.H., Rhamdhani, M.A., et al., "Thermodynamics Behavior of Germanium during Equilibrium Reactions Between FeO_x-CaO-SiO_2-MgO Slag and Molten Copper", *Metallurgical and Materials Transactions B*, Vol 47, No.5, October 2016, pp. 2889-2903.

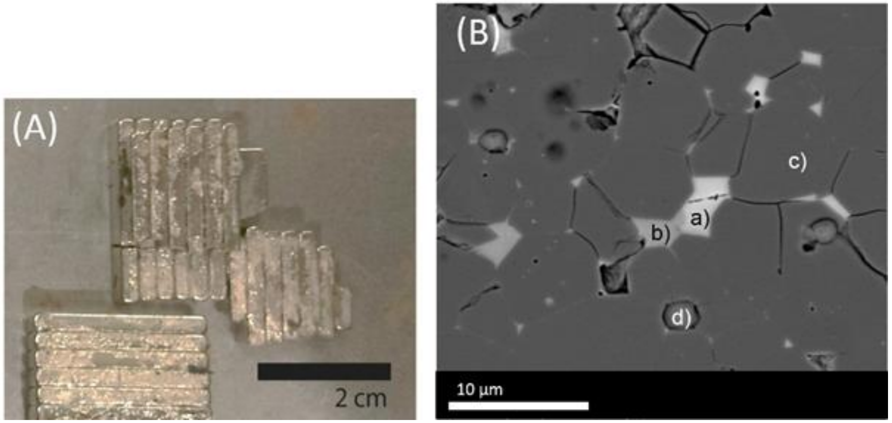
Conceptual Route for Industry



A conceptual route of e-waste recycling through black copper smelting

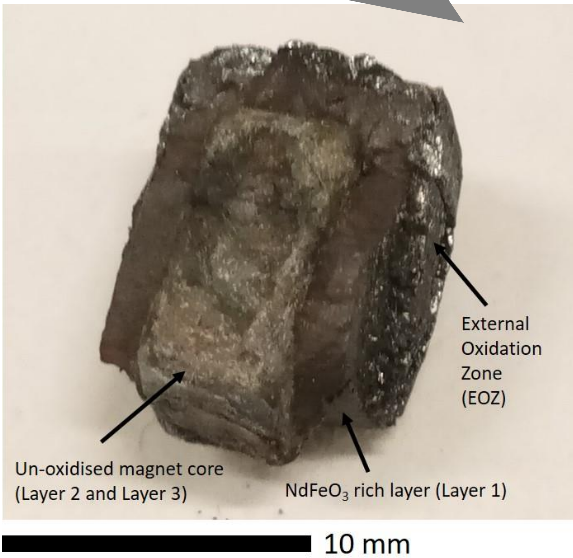
Recovery of Nd from Magnet as $NdFeO_3$

Solar Recycling of Rare Earth Elements from e-o-l Magnet as $NdFeO_3$ through Oxidation



- ➢ Waste magnet from banknote printing process supplied by Note Printing Australia Ltd.
- ➢ Bulk samples (10 x 5 x 5 mm)

- ➢ Thermally demagnetized at T = 573 K
- ➢ Discontinuous isothermal approach
- ➢ Oxidised in air



Oxidised in air atmosphere at 1373 K, ~27 h

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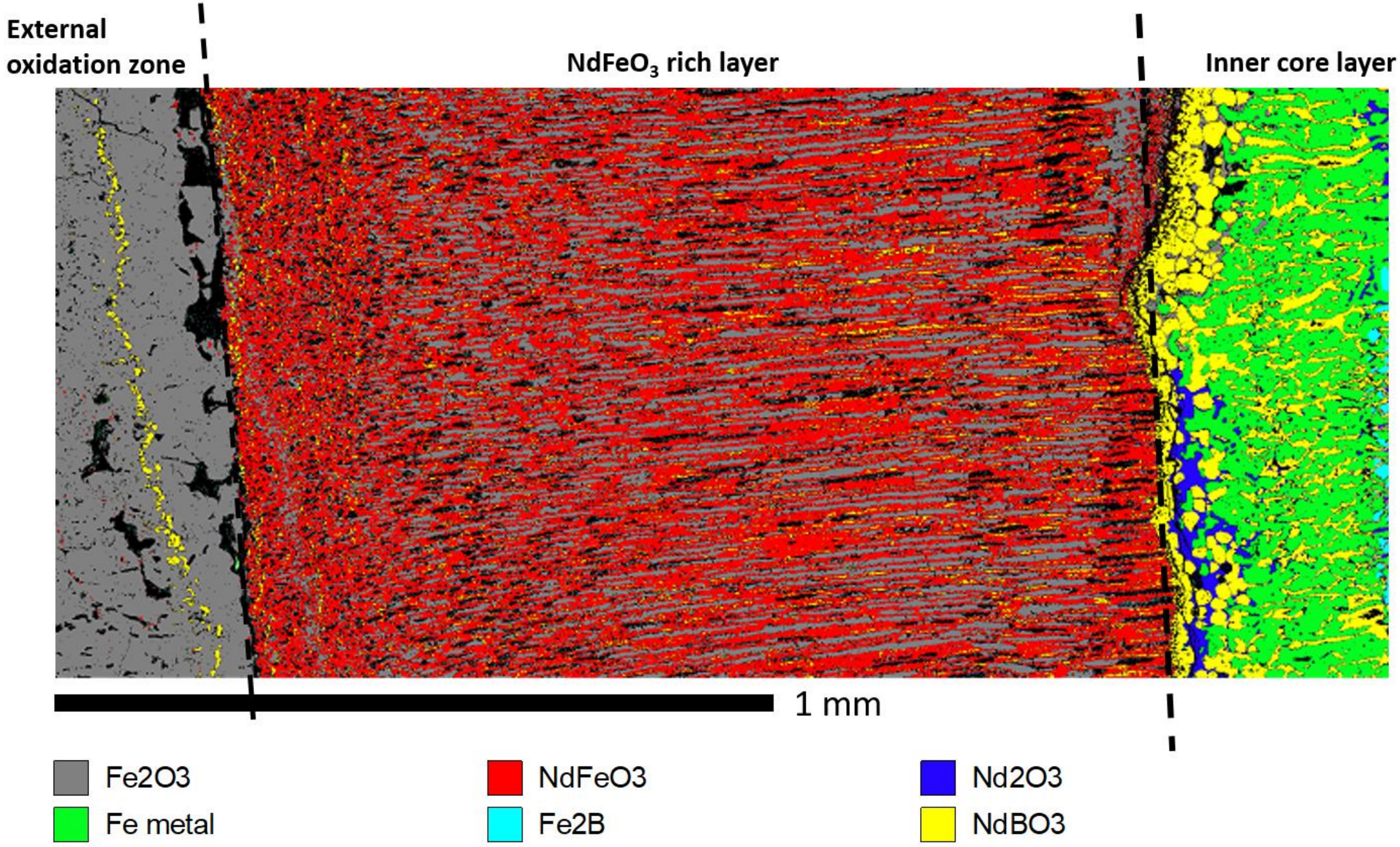
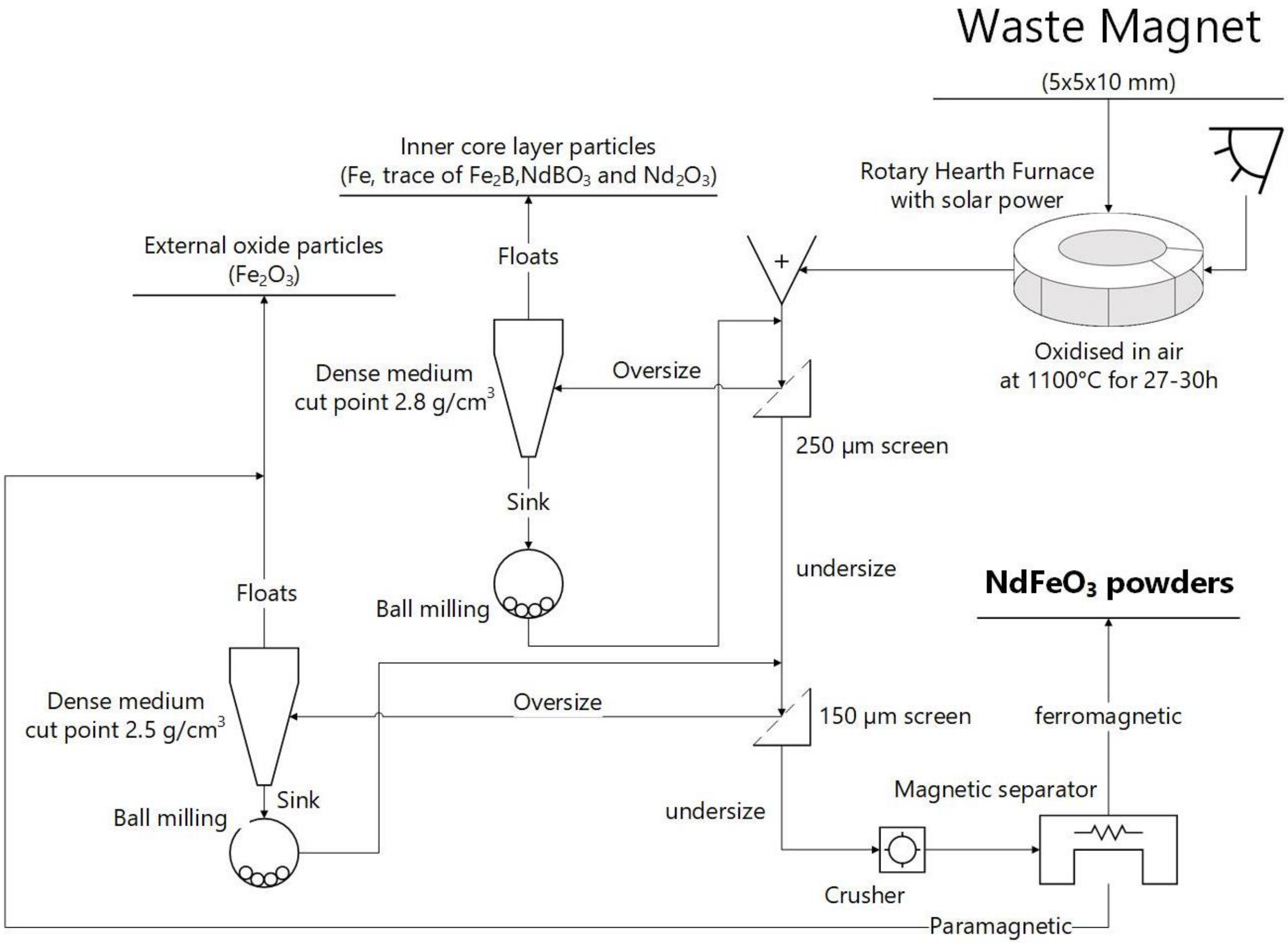


Solar Recycling of Rare Earth Elements from Magnet as $NdFeO_3$ through Oxidation



High Temperature Recycling of Alkaline Batteries

Waste

Shredded batteries

Flake C/plastic from Li-ion batteries

Black mass
Low grade materials containing zinc oxide, manganese oxides, electrolyte

Zn/ZnO Powders
$65-$1000/kg, depending on size and purity

Concluding Remarks

- Large potential for processing of **Urban Ores**

- There are **technical** and **non-technical** challenges for a sustainable processing of the alternative resources

- Need of a comprehensive approach addressing both of these challenges
  - Innovations in all sectors from **science**, **technology**, **social**, **governmental policy** to business will be vital in promoting the use of the alternative resources for maximized resource efficiency and wealth generation
  - **Need expertise from different disciplines!!!!!!**

- Optimised processing route will depend on a number of things that include the actual product, location, and other non technical aspects

Thank You !!!!!

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