Stimulation of Substitution within a Circular Economy perspective, in the metals sector: *concepts and examples*

University of Antwerp: Wednesday 7 November 2018

METALLO
THE FURNACE OF INNOVATION

METALLO
THE FURNACE OF INNOVATION

Bismuth challenging the recycling of Copper and the metal primary balance

Dirk Goris, Metallo Belgium

2018.11.07

Metallo

One group, two sites

- Founded in 1919
- 782 Million EUR of revenue in 2016
- 430 employees at Metallo Belgium and 85 employees at Metallo Spain
- 40% of growth in workforce in last 10 years

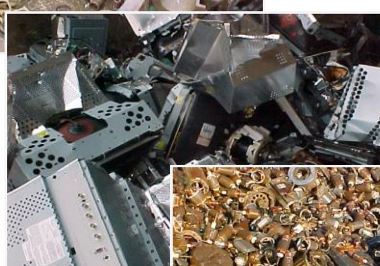
We are an international company, that excels in **recycling** and **refining** non-ferrous materials.

Metallo

Waste services

We treat the most **complex** secondary raw materials purchased **globally**. Over 350,000 tons of these raw materials are recycled annually through the different stages of our recycling processes.









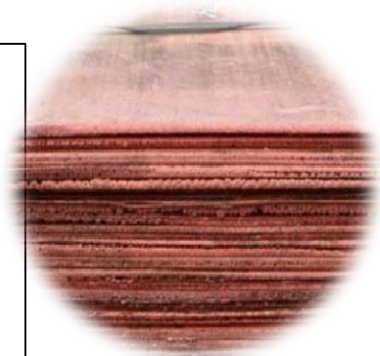
Metallo

Product range

We combine our **unique technology** and **know-how** to provide a variety of non-ferrous metal products, intermediates and minerals to our customers.

Refined metals

- ***Cu cathodes "B grade"***
  min. 99,97% Cu
- ***Sn ingots "MC brand"***
  LME registered , Low Lead , CFSI compliant "conflict free", min. 99,95% Sn
- ***Pb ingots "MC brand"***
  soft lead min. 99,9% Pb and hard lead on customer specifications



Copper cathodes
Quality: 99,98 % Cu

Hard lead
Custom made Lead Antimony alloys

Lead ingots
Quality: 99%

LME Certified
Tin ingots (MC Brand)
Quality: 99.96% Sn

Metallo

Product range

We combine our **unique technology** and **know-how** to provide a variety of non-ferrous metal products, intermediates and minerals to our customers.

Intermediates

- ***Cu anodes and Cu blister***
  ca. 99% Cu on customer specifications
- ***Anode sludges***
- ***Nickel Sulphate Solution***
- ***Nickel Briquettes***
- ***Zinc Oxides***

Copper anodes
Quality: 99 % Cu

Anode slimes
Quality: 0,5% Ag, 0,05% Au

Nickel briquettes
Quality: 90% Ni

Nickel Bleed
Quality: 5% Ni

ZnO-dust
Quality: 45% Zn

Metallo

Product range

We combine our **unique technology** and **know-how** to provide a variety of non-ferrous metal products, intermediates and minerals to our customers.

Minerals and granulates

- The final slag is a granulated iron silicate and is mainly used in construction or as raw material for the cement industry.
- ***METAMIX®***, Iron Silicate Slag
- ***ELMIX®***, Iron Silicate Slag
- ***KORANEL®*****,** Clean synthetic minerals for sustainable building applications

Metallo

Technology

In accordance with supplier's requirements and international standards, **samples** are taken for **high quality chemical assaying**

Our **technologies**, in most cases invented and realized by our own engineers, give us a **unique worldwide position** in the valorization of metal and metal compounds

We treat materials in a **responsible, sustainable** way and according to **'best reference standards'**

Metallo

- **We are “special” …**
  - multi-metal producer of Cu, Sn, Pb, Ni, starting from 100% “secondary” input materials
  - some unique, own desiged, production processes
  - specialized in converting low grade “complex” materials (many SVHCs, containing nearly the entire Table of Mendeljev …) completely into valuable products for others
  - “zero waste” policy
  - sourcing world wide
  - small as copper producer, but main European tin producer …

Metallo

- **… in a challenging environment**
  - The Copper industry can be affected by evaluation, authorization or restriction efforts on other substances, used in manufacturing and production of copper products
  - Examples
    - Heavy pressure on the use of Pb :
      - “ban” or restriction in some applications → substitution
      - reducing the classification cut-off percentage of Pb will influence transport and marketing of copper concentrates, intermediates, alloys …
      - copper scrap cannot be refined without making Pb containing by-products at the same time …
    - Cd, the “forbidden” element :
      - almost no “accepted” applications anymore, but what with the Cd that is already present in intermediates ?

Bismuth, challenging the recycling of Copper **and the metal primary balance, is this a right solution from a REACH-Circular Economy perspective?**

Introduction

- leaded copper alloys have historically been used for many purposes (e.g. casted components used in the potable water supply system)
- worldwide increasing pressure to remove hazardous metals, in particular lead, from both consumer and industrial applications
- some examples :
  - Europe : RoHS, REACH, IED, …
  - USA : Reduction of Lead in Drinking Water Act, January 4, 2011

    "lead free" = "not more than a weighted average of 0.25% Pb when used with respect to the wetted surfaces of pipes, pipe fittings, plumbing fitting, and fixtures."

Substitution of Pb by …

Bismuth	Silicon
❑ "bismuth bronze", "bismuth brass"	❑ "silicon bronze", "silicon brass"
❑ = copper alloy containing	❑ = copper alloy containing
❑ Bismuth : typically 1-3%, but sometimes more …	❑ Silicon : typically 2-5%
❑ Other elements such as zinc, tin, nickel, …	❑ Other elements : mainly zinc (3-22%)

Examples (not exhaustive …)

	Leaded Copper-Based		Lead-Free Copper-Based				
	C84400 Leaded Semi-Red Brass	C83600 Leaded Red Brass	C89833 Lead-Free Bismuth Brass	C89836 Lead-Free Bismuth Brass	C87850 Lead-Free Silicon Brass	C87610 Lead-Free Silicon Bronze	C87600 Lead-Free Silicon Bronze
Copper (%)	79.0 – 82.0	84.0 – 86.0	86.0 – 91.0	87.0-91.0	75.0–78.0	90.0 min	90.0
Lead (%)	6.3 – 7.7	4.0 – 5.7	0.09 max	0.25 max	0.09 max	0.09 max	
Zinc (%)	7.0 – 10.0	4.3 – 6.0	2.0 – 6.0	2.0-4.0	18.0-22.0	3.0–5.0	5.5
Bismuth (%)			1.7 - 2.2	1.5-3.5			
Tin (%)	2.3 - 3.5	4.3 – 6.0	4.0 – 6.0	4.0-7.0	0.30 max		
Silicon (%)	0.005 max	0.005 max	0.005 max	0.005 max	2.7-3.4	3.0–5.0	4.5
Phosphorus (%)	0.02 max	0.03 max	0.050 max	0.06 max	0.05 - 0.20		
Aluminum (%)	0.005 max	0.005 max	0.005 max	0.005 max			
Antimony (%)	0.25 max	0.25 max	0.25 max	0.25 max	0.10 max		
Iron (%)	0.35 max	0.25 max	0.30 max	0.35 max	0.10 max	0.20 max	
Manganese (%)					0.10 max	0.25 max	
Nickel (%)	0.8 max	0.8 max	1.0 max	0.9 max	0.20 max		
Sulfur (%)	0.08 max	0.08 max	0.08 max	0.08 max			

Why bismuth ? Why silicon ?

Bismuth	Silicon

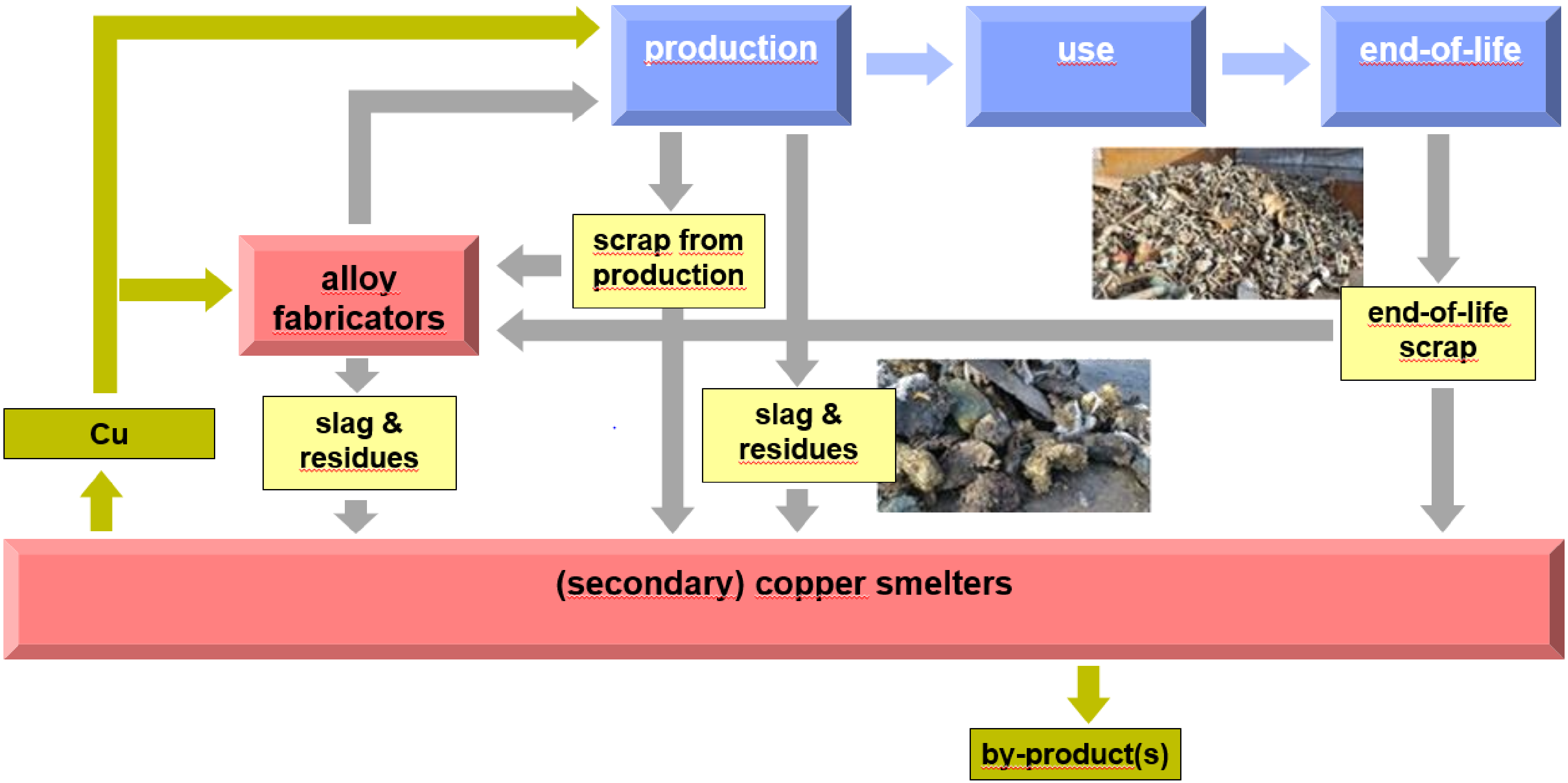
❑ "bismuth bronze", "bismuth brass"
❑ = copper alloy containing
  ❑ Bismuth : typically 1-3%, but sometimes more …
  ❑ Other elements such as zinc, tin, nickel, …
	❑ "silicon bronze", "silicon brass"
	❑ = copper alloy containing
	  ❑ Silicon : typically 2-5%
	  ❑ Other elements : mainly zinc (3-22%)

Both solutions acceptable

- **from a technical point of view ("required performance of product")**
- **from a human health point of view ("not hazardous")**

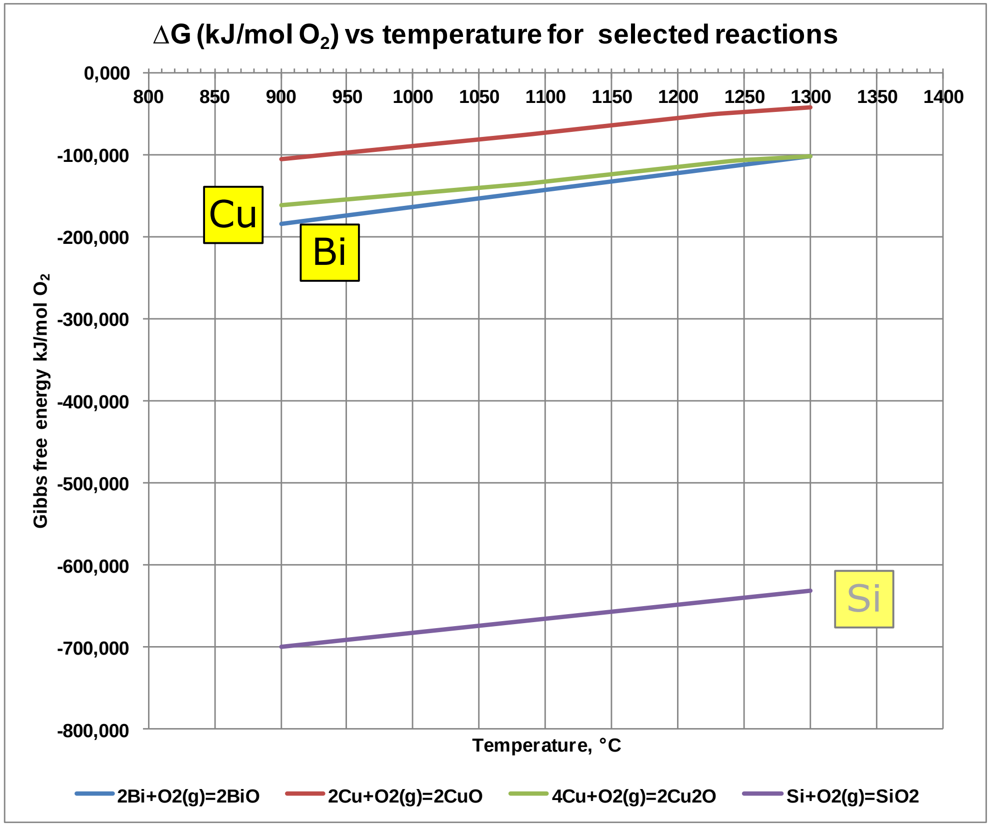
But … we have to look to the entire life cycle, and even further…

Life cycle of copper alloys



Technical feasibility during recycling

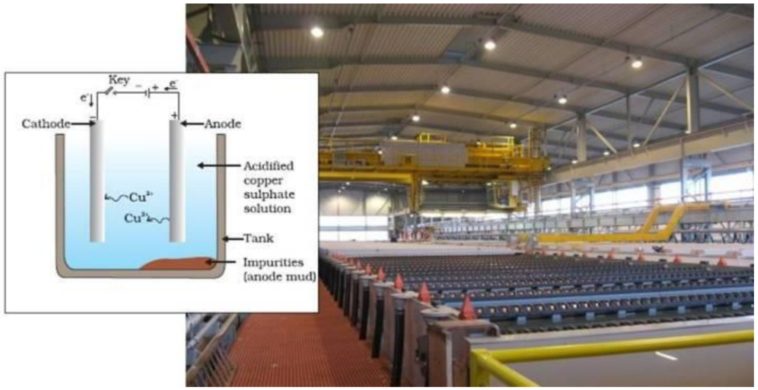
Refining of Copper - pyrometallurgy



- **Based on more/less selective reaction of oxygen with "impurities" in liquid "copper", depending on**
  - Properties of "impurity"
  - Temperature
- **Graphical presentation in "free energy" diagram : the more negative ΔG, the easier the oxidation of the element**
- **Conclusion :**
  - Bi : almost impossible to remove from copper
  - Si : easy to remove from copper

Technical feasibility during recycling

Refining of Copper - electrorefining



Electrochemical reaction	Standard reduction potential (25°C), volts
$Au^{3+} + 3e^- \rightarrow Au^\circ$	1.5
$Ag^+ + e^- \rightarrow Ag^\circ$	0.80
$Cu^{2+} + 2e^- \rightarrow Cu^\circ$	0.34
$BiO^+ + 2H^+ + 3e^- \rightarrow Bi^\circ + H_2O$	0.32
$HAsO_2 + 3H^+ + 3e^- \rightarrow As^\circ + 2H_2O$	0.25
$SbO^+ + 2H^+ + 3e^- \rightarrow Sb^\circ + H_2O$	0.21
$2H^+ + 2e^- \rightarrow H_2$	0.0000 ($pH = 0$; $pH_2 = 1$ atmosphere)
$Pb^{2+} + 2e^- \rightarrow Pb^\circ$	-0.13
$Ni^{2+} + 2e^- \rightarrow Ni^\circ$	-0.26
$Co^{2+} + 2e^- \rightarrow Co^\circ$	-0.28
$Fe^{2+} + 2e^- \rightarrow Fe^\circ$	-0.45

- **Based on more/less selective dissolution / deposition by electrical current in aqueous solution, depending on the properties of the "impurity"**
- **Indicated by "standard reduction potential" :**
  - the lower, the easier to dissolve into solution,
  - the higher, the easier to deposit from solution
- **Additional complication :**
  - formation of "floating" slime in solution → contaminating cathode
- **Conclusion**
  - Bi : difficult to remove from copper
  - Si : not relevant : Si will not "survive" the pyrometallurgical refining

Technical feasibility during recycling

Quality requirements for Copper

Element	ASTM B–115 Grade 1	ASTM B–115 Grade 2	BS EN 1978	IWCC High Grade
% Cu+Ag		99.95		
Se (ppm)	2	10	2	2
Te (ppm)	2	5	2	2
Bi (ppm)	1	3	2	2
Bi+Se+Te (ppm)	3		3	3
Sb (ppm)	4	15	4	4
Pb (ppm)	5	40	5	5
As (ppm)	5	15	5	5
Fe (ppm)	10	25	10	10
Ni (ppm)	10	20		
Sn (ppm)	5	10		
S (ppm)	15	25	15	15
Ag (ppm)	25	70	25	25
Co (ppm)				
Mn (ppm)				
Zn (ppm)				
Total (ppm)	65		65	65

- **Properties of "copper" are affected by impurities**

  → limitations, "standards"

- **Customers usually require purer copper than listed in the standards**

- **Main effect of Bi : grain boundary embrittlement**

- **General conclusion :**
  - Detrimental for wire drawing applications
  - Bi content should be reduced to < 1 ppm

Technical feasibility during recycling

Implications for Copper smelters & refiners

- **most final products are made from copper cathodes**

- **because of contamination of cathodes from Bi in anodes**

  → **limitation on Bi content of copper anodes (indication : 50-200 ppm)**

- **because of limited refining capacity by oxidation (in producing anodes)**

  → **dilution required at input**

- **dilution requires more detailed knowledge on input composition**

  → **requires severe efforts on quality control of input material**

Technical feasibility during recycling

Implications for smelters & refiners

- most final products are made from copper cathodes
- because of contamination of cathodes from Bi in anodes
  → limitation on Bi content of copper anodes (indication : 50-200 ppm)
- because of limited refining capacity by oxidation (in producing anodes)
  → dilution required at input
- dilution requires more detailed knowledge on input
  → requires severe efforts on quality control of input material

Technical feasibility during recycling

Quality control of input (1)

- **vital aspect for economical and technical performance of the smelter**

- **purchase price of raw materials (scrap, slag, residue, …) is affected by Bi content**
  - Bismuth is penalized by all copper smelters, reflecting the technical difficulty to separate bismuth from copper
  - When the Bi content exceeds a certain limit value, the material can even be refused

- **quality control on slag & residues ranges from**
  - "easy" for relatively homogeneous material by common practice of sampling and assaying according to "good practice" procedures
  - to "very difficult" for very heterogeneous materials,
    - requiring technical treatments as sorting out (based on visual interpretation), seiving, crushing, grinding, …
    - requiring right interpreation of visual aspects

Technical feasibility during recycling

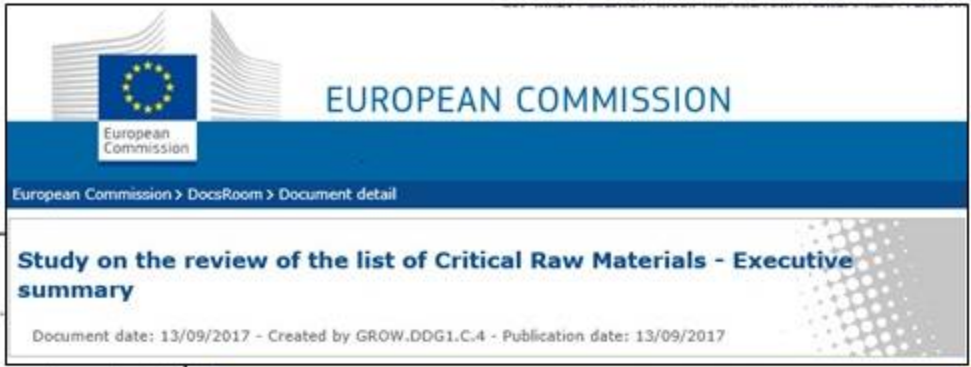
Quality control of input (2)

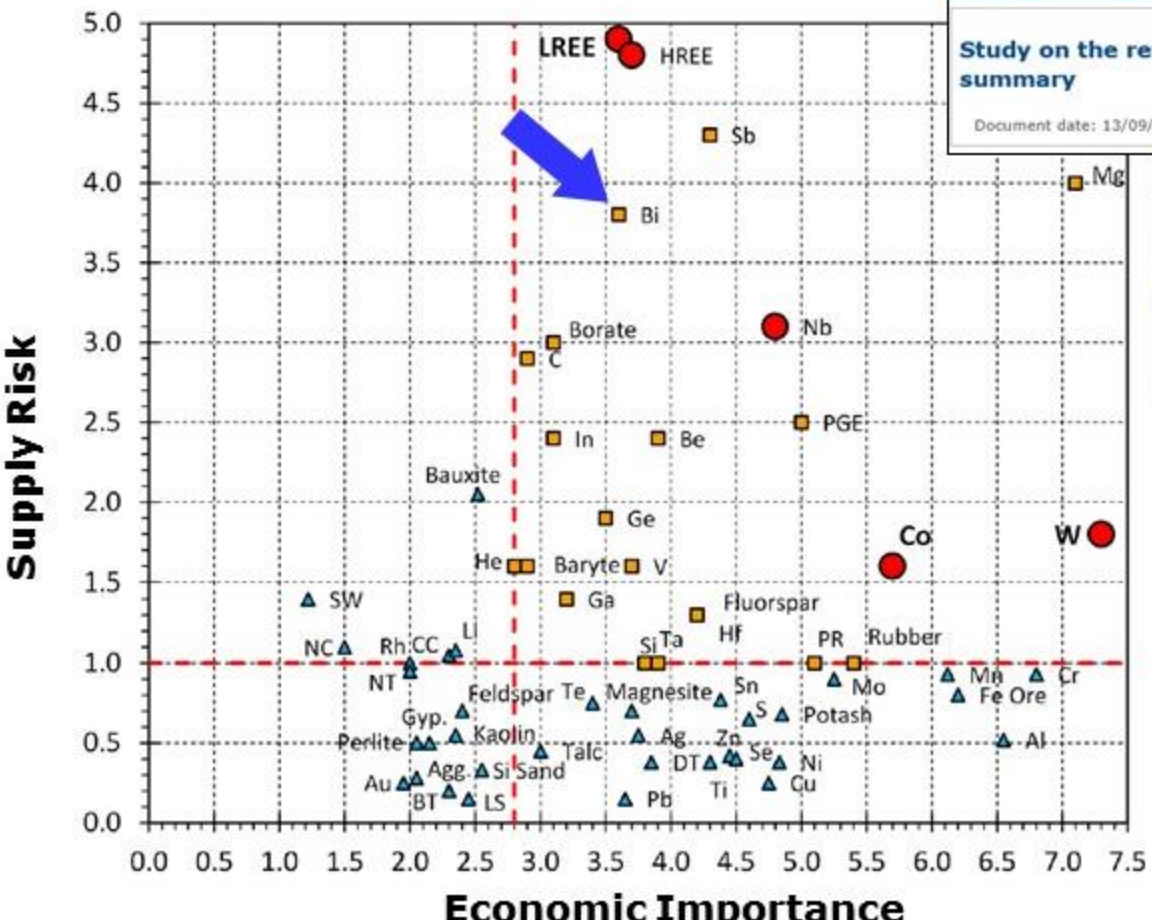
- **quality control of scrap :**
  - Often combination of
    - visual inspection
    - recognition of distinctive articles with their known composition in the scrap (based on assays and historical data)
    - estimation
  - Usually only focussed on some main elements
  - If harmfull elements are expected, much more time and efforts are needed to quantify them
    - To safeguard the refining process
    - To safeguard the final product specifications
  - However : representative sampling ???

(Natural) availability

	Bismuth	Silicon
elemental abundance		
ranking	69th place	2nd place
concentration (crust)	8 ppb = 0.0000008 %	28%
production		
world	2016 : 17100 t	2016 : ca. 2780000 t
USA	2016 : 0 t	2016 : 310000 t (incl. FeSi)
main producers	China, Laos, Mexico, Japan	Australia, Brazil, Canada, South Africa, Norway
source	mainly as by-product of lead refining …	direct smelting and reduction of quartz
consumption		
USA	2016 : 733 t (reported), 1670 t (apparend)	2016 : > 200000 t (incl. FeSi)

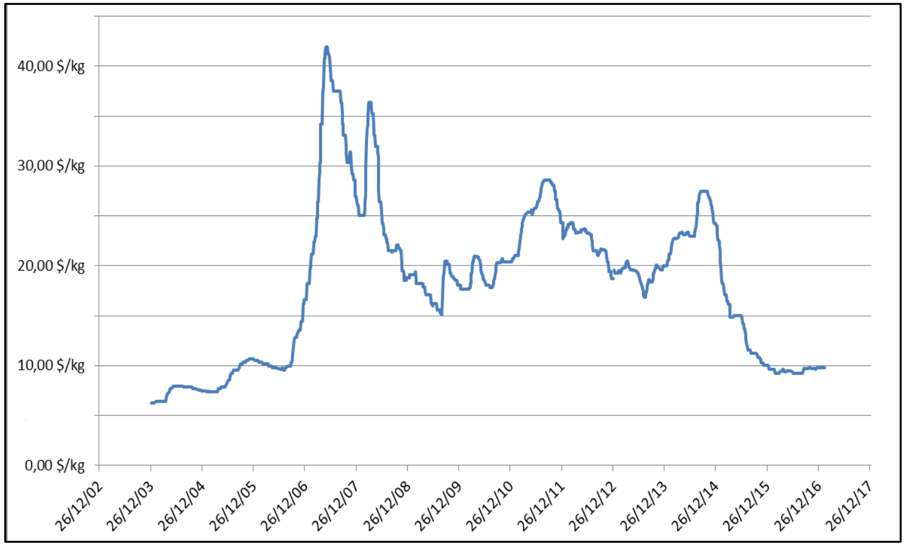
(Natural) availability

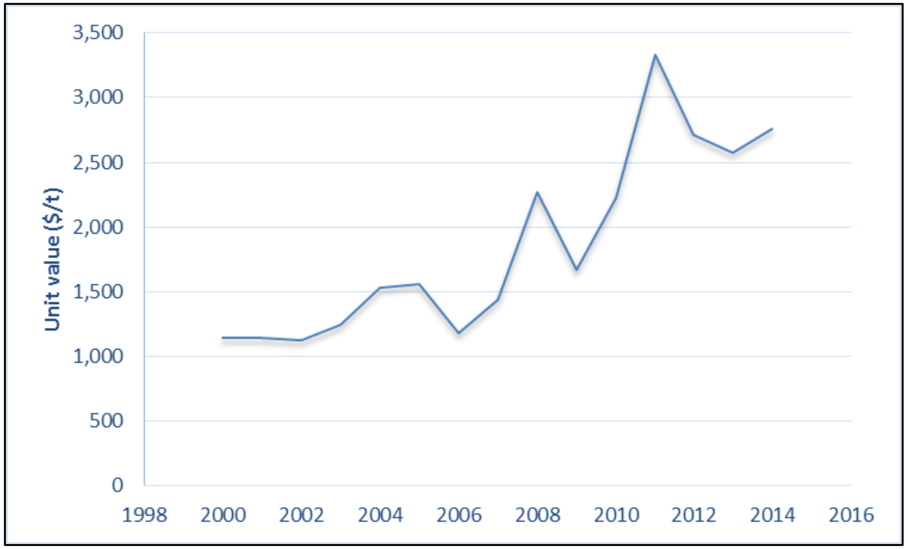




2017 Critical Raw Materials (26)			
Antimony	Gallium	Magnesium	Scandium
Baryte	Germanium	Natural graphite	Silicon metal
Beryllium	Hafnium	Natural Rubber	Tantalum
Bismuth	Helium	Niobium	Tungsten
Borate	HREEs	PGMs	Vanadium
Cobalt	Indium	Phosphate rock	
Fluorspar	LREEs	Phosphorus	

Availability is reflected in metal price…





Bismuth

2011	**24000 $/t**
	17589 €/t
2014	**10000 $/t**
	8660 €/t

high volatility

Silicon

2011	**3200 $/t**
	2345 €/t
2014	**2800 $/t**
	2430 €/t

moderate volatility

General overview

	Bismuth	Silicon
technical level of difficulty		
quality control	difficult/time-consuming	not relevant
refining	difficult / by dilution	easy
availability	scarce	abundant
impact on market	high (price increase , substitution, …)	low
economics		
metal price	high	low
purchase scrap	penalties / refusal	no effect

Conclusions

- **Bi may be an acceptable substitute for Pb in Cu alloys from the point of view from manuafacturing and downstream use …**

- **…but has some other drawbacks :**

  - **Economic feasibility may be a challenge due the limited availability (REACH)**

  - **Each additional ton of Bi requires >100 t Pb to be recovered from primary resources (Sustainablility)**

  - **Technical feasibility of recycling will be significantly jeopardized (no "design for recycling"…) (Circular Economy)**

QUESTIONS ?