



Refractory metals: Industrial waste resources

Xianfeng Hu, Lena Sundqvist Ökvist and Guozhu Ye
Swerea MEFOS

Based on contribution from REFRAM partners

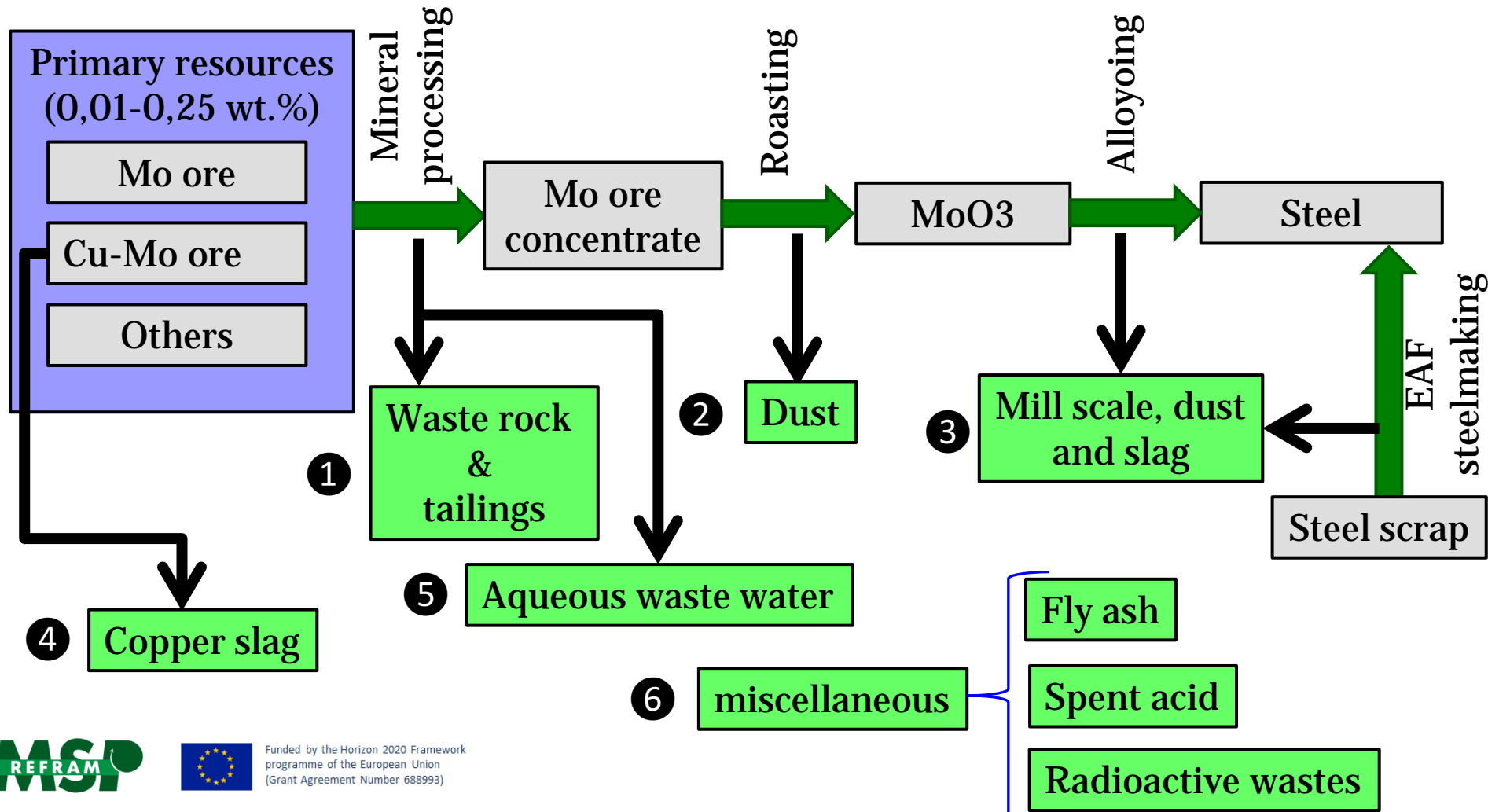
9-10 March, 2017



Funded by the Horizon 2020 Framework
programme of the European Union
(Grant Agreement Number 688993)

1 Mo: industrial waste resources

❖ What are they and where are they from?



❖ Generation and properties of the industrial waste resources

- **Waste rock:**
coarse, crushed, or blocky materials covering a range of particle sizes;
- **Mill tailings**
mainly very fine particles rejected from the grinding, screening, or processing of the raw materials.

Waste rock dump: an example

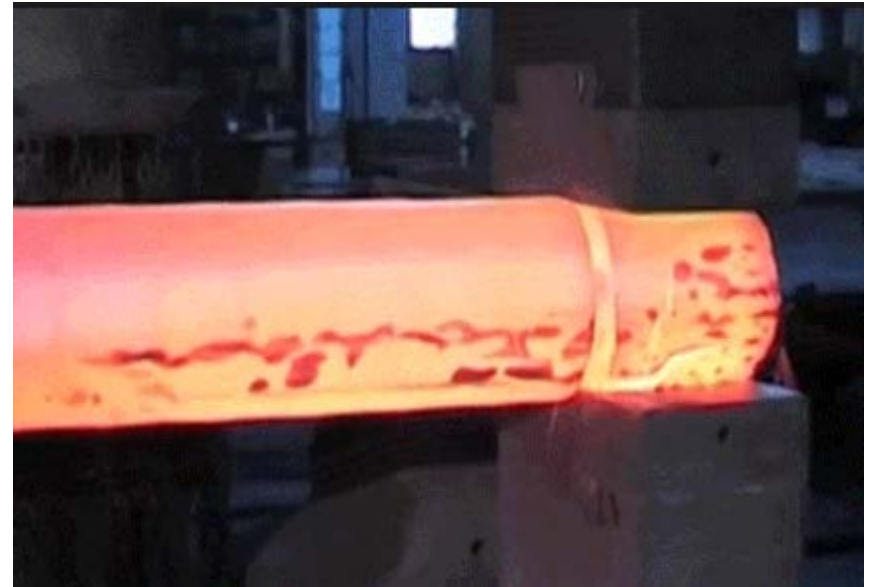
The grades of Mo in waste rock and tailing varies with the sources but are normally very low.

- **Steelmaking dust**

- Generated in the steelmaking plants (EAF, AOD, etc.);
- Mo contents in the dust vary with the types of the produced steel.
- The amount: ~ 20 kg/ton of the steel from the EAF steelmaking process.

- **Mill scale**

- Generated in the hot metalworking process, such as casting, hot rolling/ forging, etc.
- Mo contents in the mill scale also vary with the types of the produced steel;
- The amount: ~ 20 kg/ton of the steel to be processed.



Mill scale generation during the forging process

Since the Mo is largely used to produce carbon steels with 0.2-0.5% Mo, the grades of Mo in the mill scale are normally very low.

- **Copper slag**

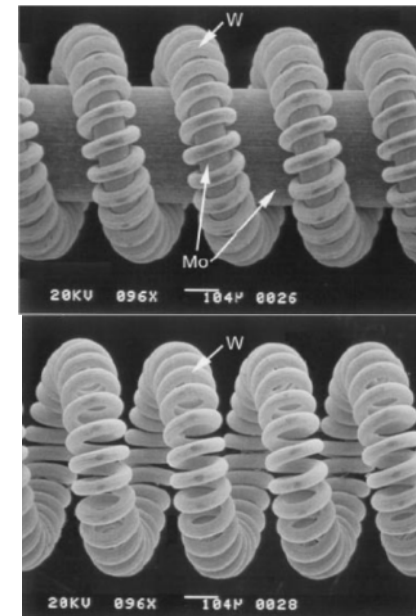
- Generated in smelting reduction process of Mo-containing copper sulfide ores;
- Mo contents can be as high as 0.3% in some cases.

- **Mo-containing spent acid.**

- Generated in the incandescent lamp making industries;
- Containing 40-70 g/L of molybdenum;
- Averagely generating 300 to 800 liters per day, which amounts to 20 to 50 kg of Mo per day.

- **Fly ash**

- Generated in the power stations;
- Containing ~ 5.0% V , ~ 1.54% Ni and 0.35% Mo from heavy oil fired power stations.

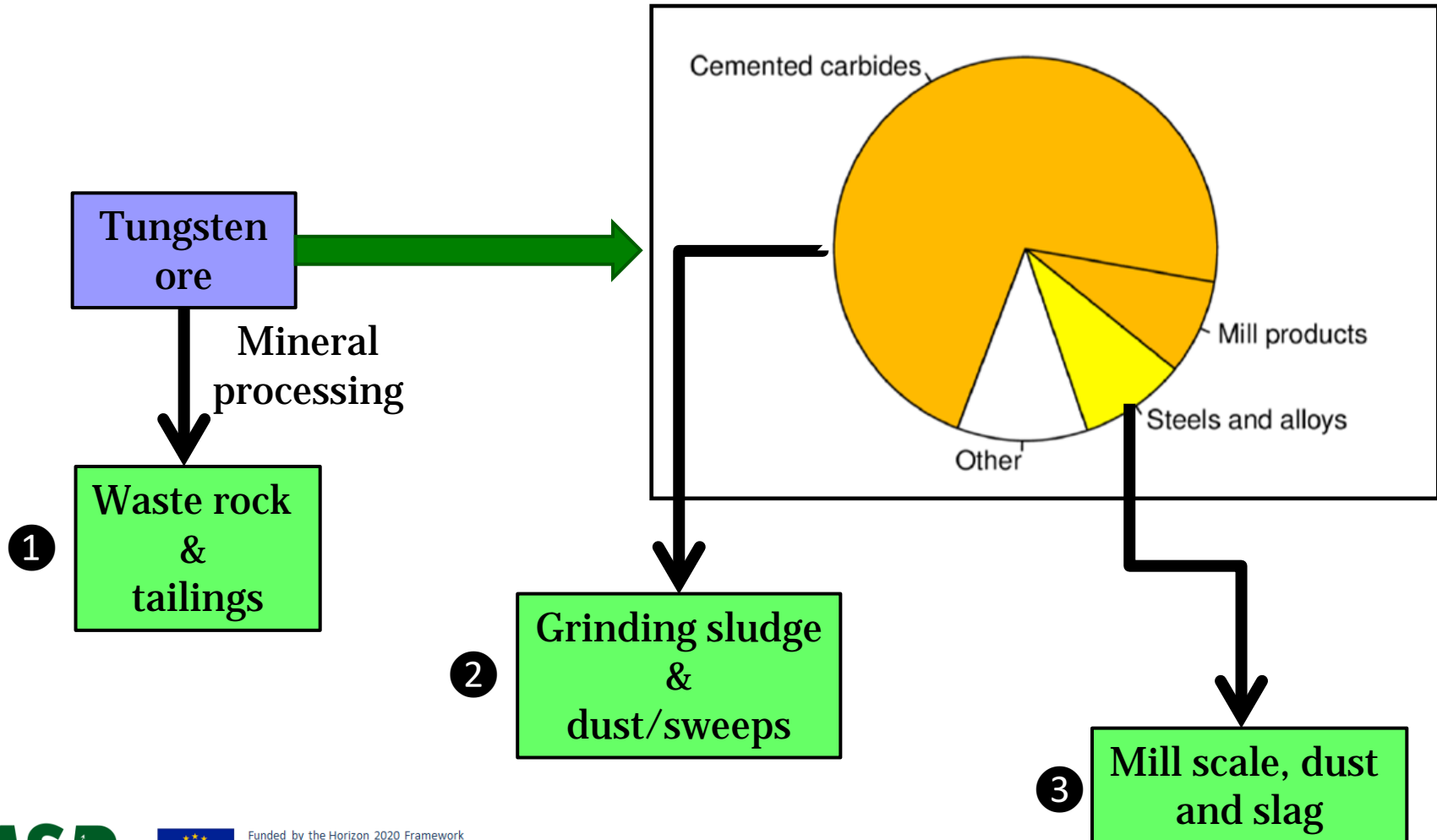


W coil on Mo mandrel (before and after acid dissolution of Mo)

- **Aqueous waste water from flotation mills**
 - Generated in copper, molybdenum and uranium flotation mills;
 - Grades vary with the sources, for example: Containing 1 - 30 mg/L in **Cu mine** in Arizona, 900 mg/L in **uranium mill** in Colorado; 25 mg/L in **Mo mills** in Colorado
- **Radioactive wastes from Mo/Tc generators production**
 - Generated during the production of generator systems;
 - In the form of solids, liquids and gases.

2 W: industrial waste resources

❖ What are they and where are they from?



❖ Generation and properties of the industrial waste resources

• Waste rock and tailings

- Generated during the mineral processing;
- Including old and new dump waste rock/tailing;
- W grades vary with the sources, but normally **very low**.

Examples:

- Panasqueira mine in Portugal

Total tailings volume:

Rio tailings (1.2 million m³)

Barroca Grande (7 million m³)

Average W content: 2.4 mg/kg

- La Parrilla mine tailings in Spain

Total tailings volume:

1.2 million m³

Average W content: 2.8 mg/kg

Amount W produced: 113 t of 60 % WO₃ in 2014

(Target: 25 t/month)

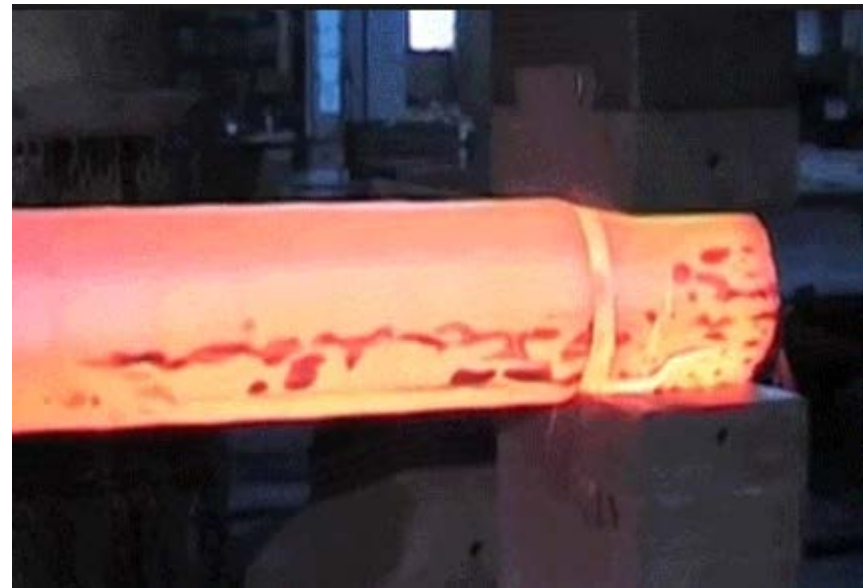


- **Grinding sludge & dust/sweeps**
- Generated during grinding, cutting, shaping, forming and finishing of the manufacturing of tungsten carbide tooling, inserts and wear parts and other carbide items.
- W grades vary with the sources, but normally **very high**.

Type	W concentrate, wt.%
W grinding sludge	30-60
W cutting sludge	70-80
Hard metal grinding sludge	15-60
Swarf	92-97
Sweepings	40-60

- **Mill scale & dust**

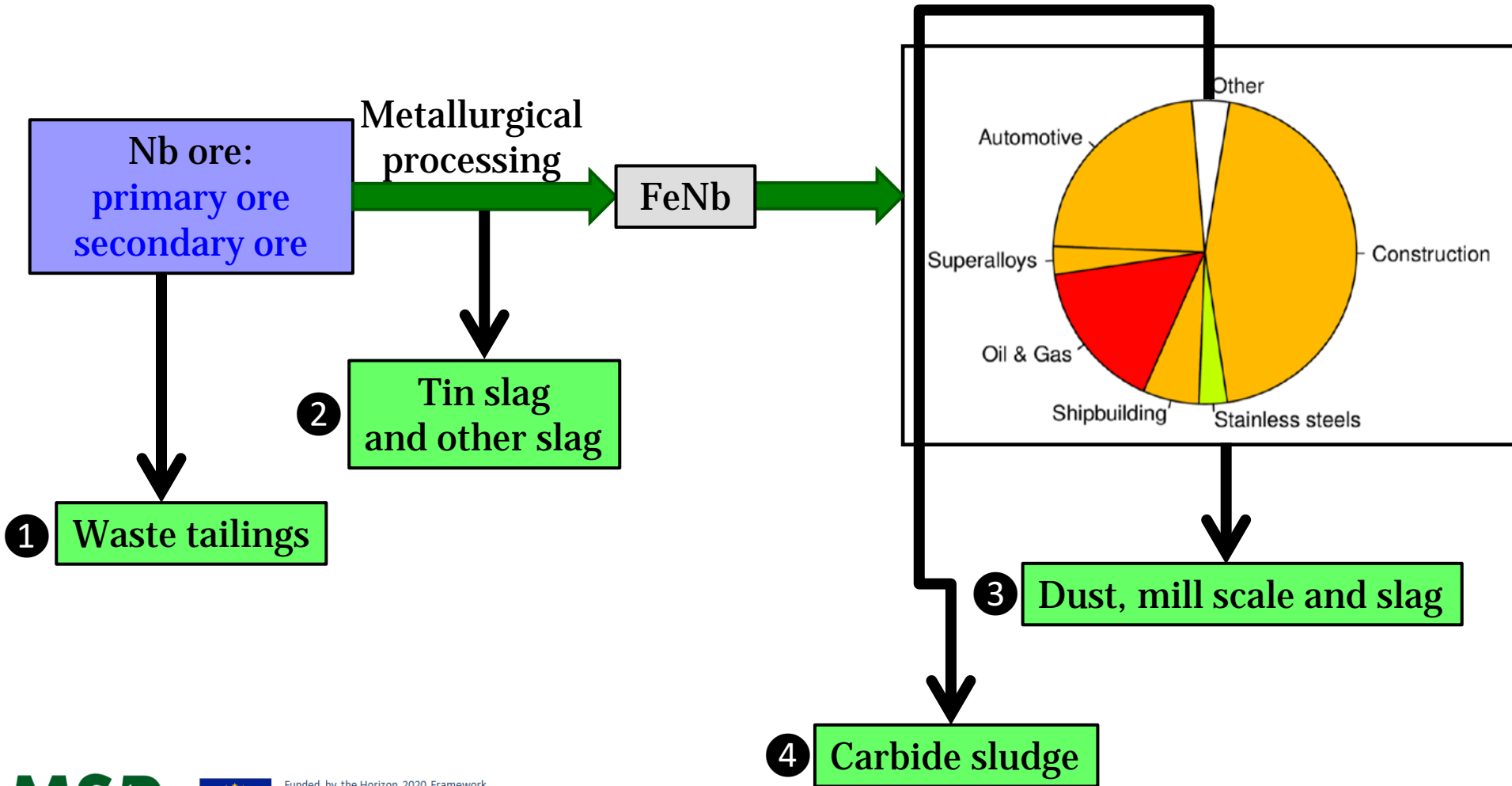
- Generated during the steelmaking process.
- Have similar chemical composition as steels (other than oxygen);
- Amounts to approx. 2 % of steel production ;
- Usually recycled internally as raw material (big plants);
- Landfill (small plants);
- W content (1 – 5 %).



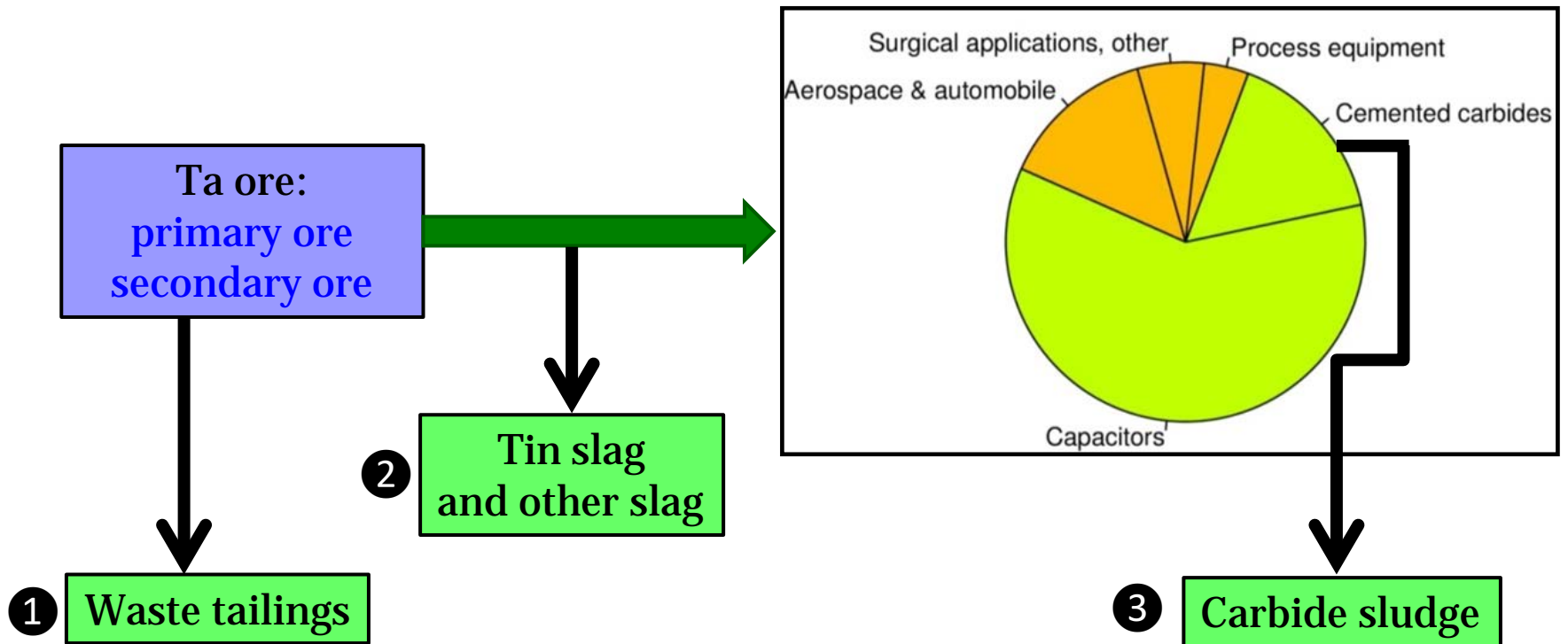
Mill scale generation during the forging process

3 Nb and Ta: industrial waste resources

❖ Industrial waste for Nb



❖ Industrial wastes for Ta



❖ Generation and properties of the industrial waste resources

• Waste tailings for Nb

- Generated during the mineral processing;
- Nb grades are in several or several tens of ppm;

Examples:

Type of Material	Company/ Mine	Location	Grade of Mo	Reserve, Mineralogy and Characterization	Ref
Waste tailing	Kiruna and Svappavaara Mine	Sweden	11.9 pm	Iron mine Other minerals: Cu, Nb, Ni, Pb, V, W, Zn...	[18]
Mine waste dump	Buchim Mine	Macedonia	2.5 ppm	Active plant Surface storage. 46409630 m ³ Mineralogy: Chalcocite- Chalcopyrite-Covellite- Cuprite-Galena-Hematite- Goethite (limonite)- Magnetite-Pyrite-Sphalerite- Tenorite-Native metal	[20]

• Waste tailings for Ta

- Generated during the mineral processing.

Examples: Tailings and waste in Penouta mine in Spain is one of the most potential old waste areas

- 5 Mt tailings containing **48 g Ta/ton** and 390 g Sn/ton
- 6.8 Mt waste containing **27 g Ta/ton, 29 g Nb/ton** and 460 g Sn/ton

Other waste tailings can also be found at Golbejas, Spain; Vieiros, Portugal; Echassiers, France

• Tin slag for Nb and Ta

- Generated during the Tin smelting ;
- (Nb + Ta) can be as high as > 10%;
- Nb produced in this way accounts for 2% of Nb production.
- Ta produced in this way accounts for 10-20% of Ta production.

- **Nb-containing dust, mill scale and slag from steelmaking process**
 - Generated during the EAF steelmaking process;
 - Believed to be in large amount but in low grades;

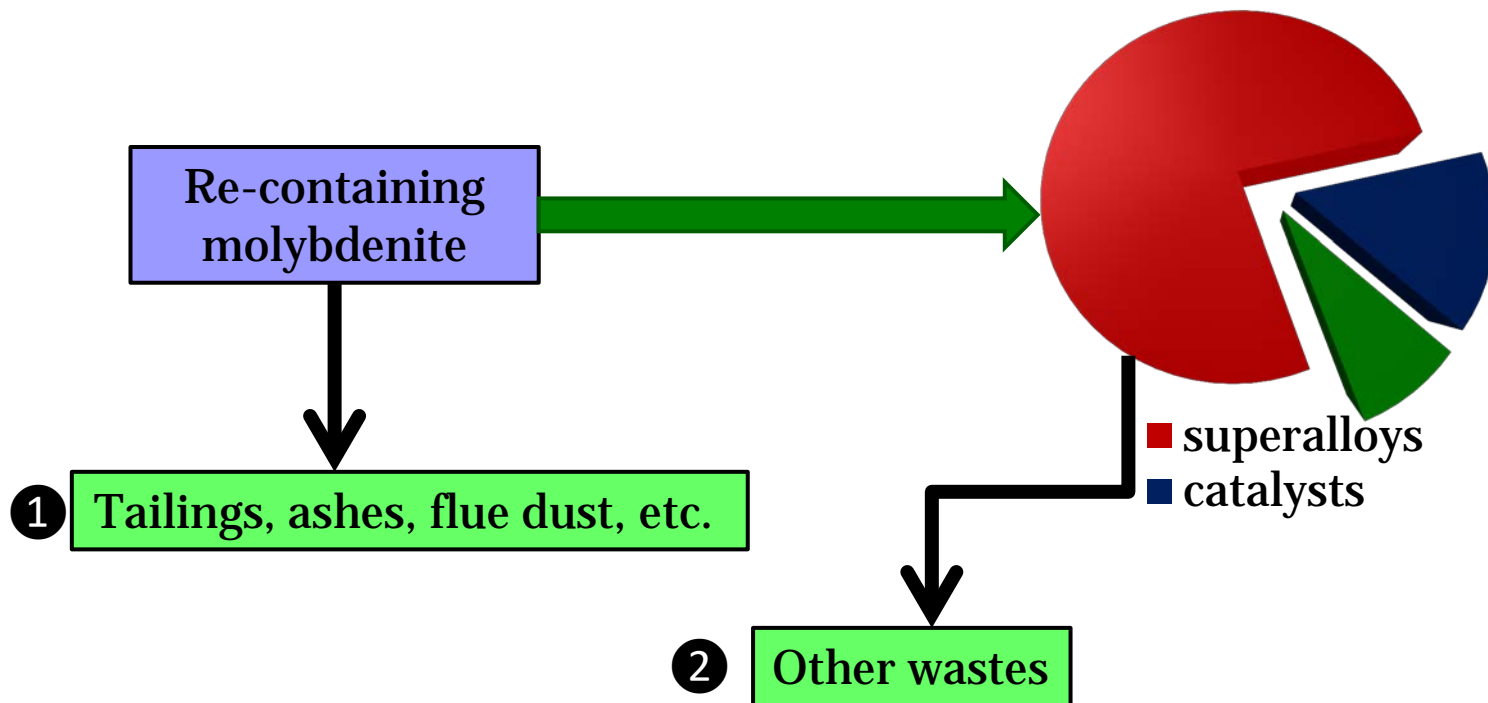
Important fact:

- Nb is largely used to produce steels, especially HSLA steels.
- Nb in the steel is normally very low:
 - HSLA steels contain ~0.05% Nb;
 - Stainless steels contain 0.04-0.08% Nb;
 - Superalloys contain 3-5.5% Nb.
- Nb is very easy to be oxidized and lost in the **slag and dust** during melting steel scrap in the EAF.
- 2% of mill scale is generated during hot metalworking of the steels.

- **Nb/Ta-containing carbide sludge**
- Generated during the Tin Nb/Ta-containing cemented carbide production;
- Believed to be in small amount for Nb but larger amount for Ta;
- **Miscellaneous**
 - **MSW incineration waste:** 61 000 t/d in EU– estimate 3-5 mg Ta/kg;
 - **Industrial landfills**, especially WEEE wastes;
 - **Municipal landfills:** low Ta concentrations, about 1 mg/kg.

4 Re: industrial waste resources

- ❖ What are they and where are they from?



❖ Typical Re-containing industrial waste resources

Type of Material	Company/ Mine	Location	Grade of Re	Reserve, Mineralogy and Characterization	Ref
Flue dust (pyrometallurgical, electrochemical processes)	Mansfeld (smelter)	Germany	63 g/t	Surface Storage 257 000 m ³ Anglesite-Galena- Quartz-Sphalerite- Wurtzite-Acanthite- Augite-Boléite-Bornite- Chalcopyrite-Digenite- Fayalite-Galena- Hardystonite-Melilite- Sphalerite-Djurleite	[20]
Tailing waste	Iberian Pyrite Belt	Portugal	3.4 ppm	Abandoned pyrite mine	[41], [42]
Tailing and ash	Asarel Mine	Bulgaria	0.05 µg/g ash	In operation. Cu extraction and processing factory	[43]
Waste tailings Waste rock	Aitik Mine	Sweeden	1587ppm	26 000 waste rock (65% deposited separately for alternative use) Tailing produced of 35 676 Ktonnes	[35], [18]

Thank you!