

Economia circolare nella produzione industriale del metallo duro: un esempio di collaborazione tra industria e ricerca privata

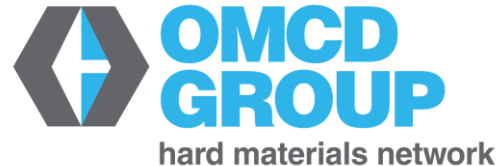


Gian Pietro De Gaudenzi^(a), Alfonso Nardelli^(b)

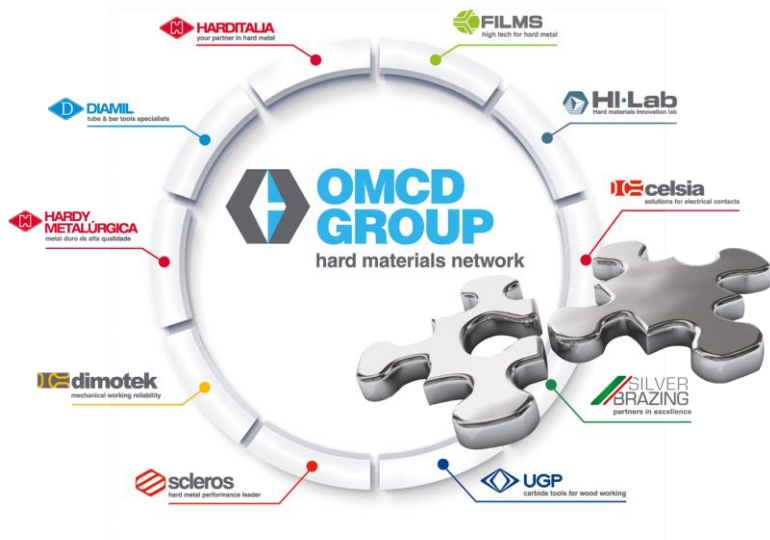
(a): F.I.L.M.S. S.p.A., OMCD Group

(b): SERICHIM s.r.l.

TUNED SYNERGY
FOR THE **BEST**



Outline



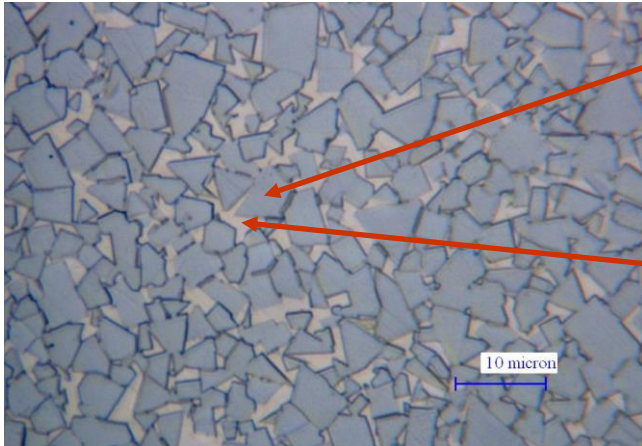
275 employees

51 M€ turnover

- ✓ The co-operation between **FILMS S.p.A.** (OMCD Group) and **Serichim S.r.l.**
- ✓ **Hardmetals** and the need to recycle **Critical Raw Materials**
- ✓ The Production Process and **Circular Economy model** of the OMCD Group
- ✓ Where are we going

Hardmetal

Composite material, where carbide (mainly **WC**) particles are cemented by a metallic matrix (mainly **Co** based), produced by a PM process through Liquid Phase Sintering (LPS)



Carbides: **WC**,
TiC, TaC,
NbC, Mo₂C



hardness

700 ÷ 2400 HV30

81.0 ÷ 94.5 HRA

Metallic matrix: **Co**,

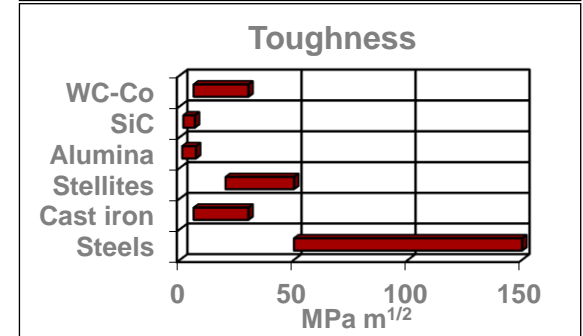
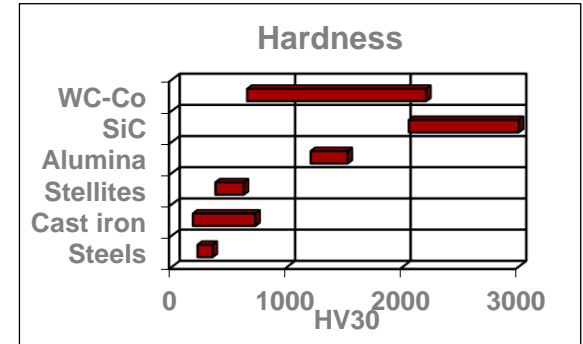
Ni, Fe

Cr, V



toughness

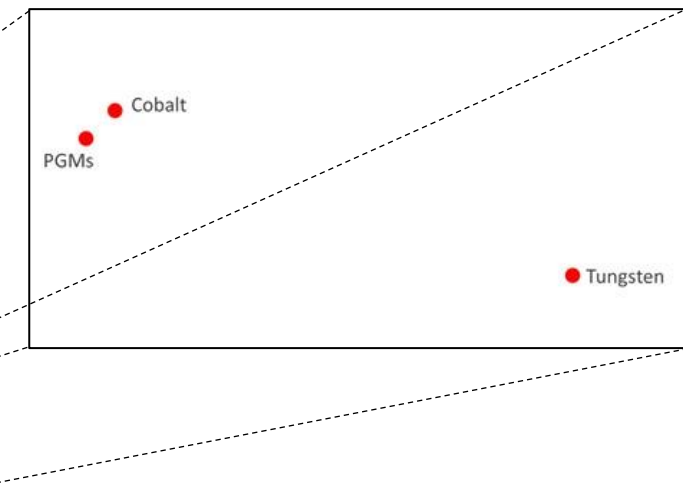
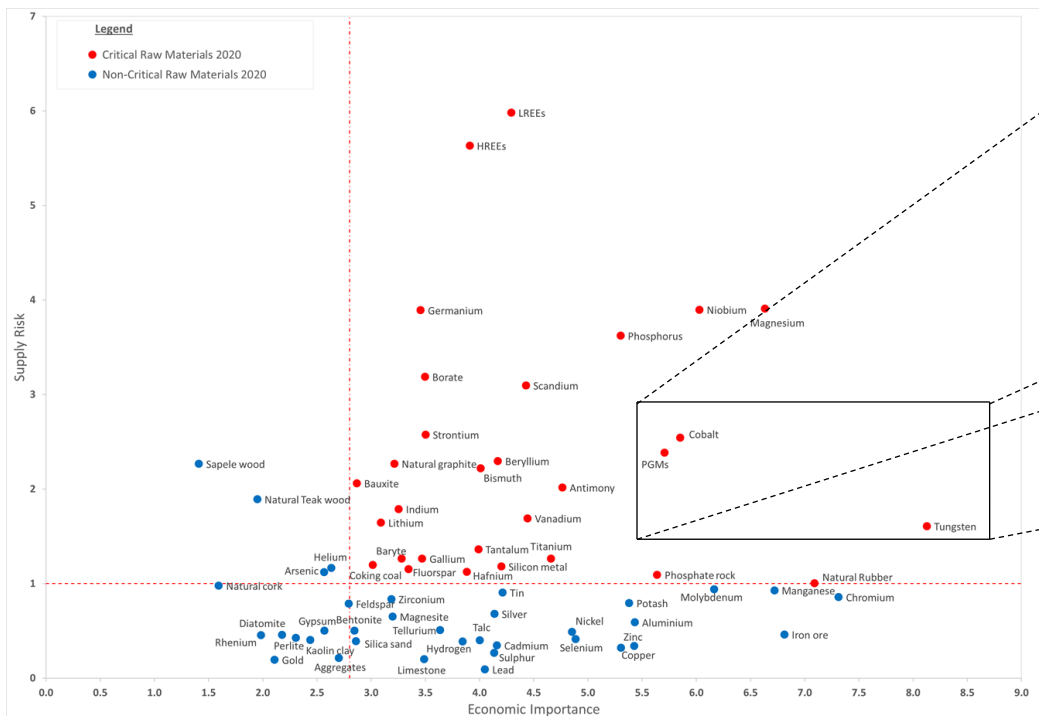
5 ÷ 30 MPa·m^{1/2}



source: Understanding Cemented Carbides, Sandvik Hard Mat:s

W and Co: Critical Raw Materials (CRMs)

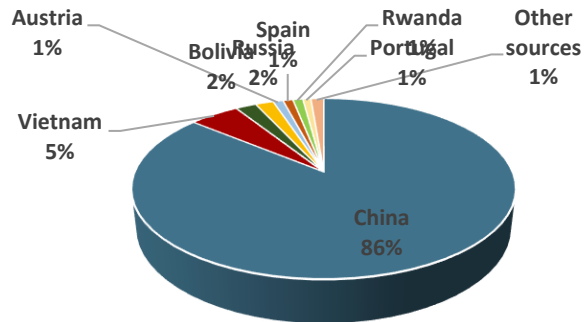
European Commission: 2011 to 2020 List of **Critical Raw Materials** (30 CRMs)



source: <https://rmis.jrc.ec.europa.eu/?page=crm-list-2020-e294f6>

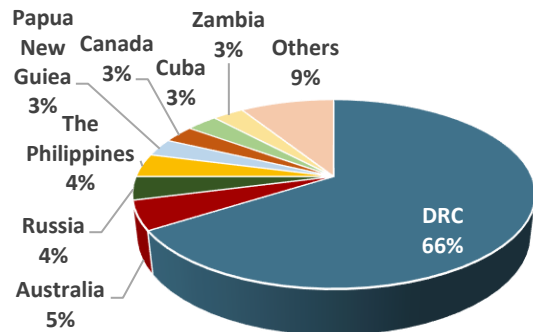
W and Co: mine production and recycling

W



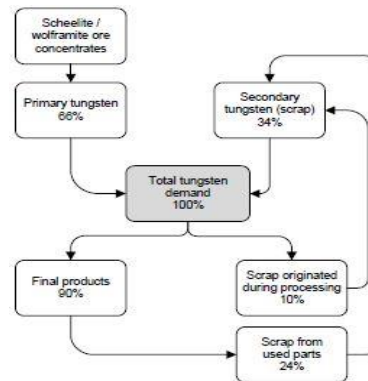
Mine Production 2020: 82785 t

Co



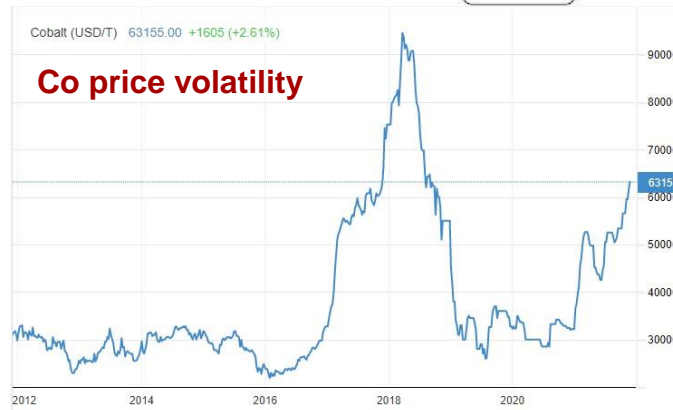
Mine Production 2020: 140000 t

35-40% W is recycled as a secondary RM



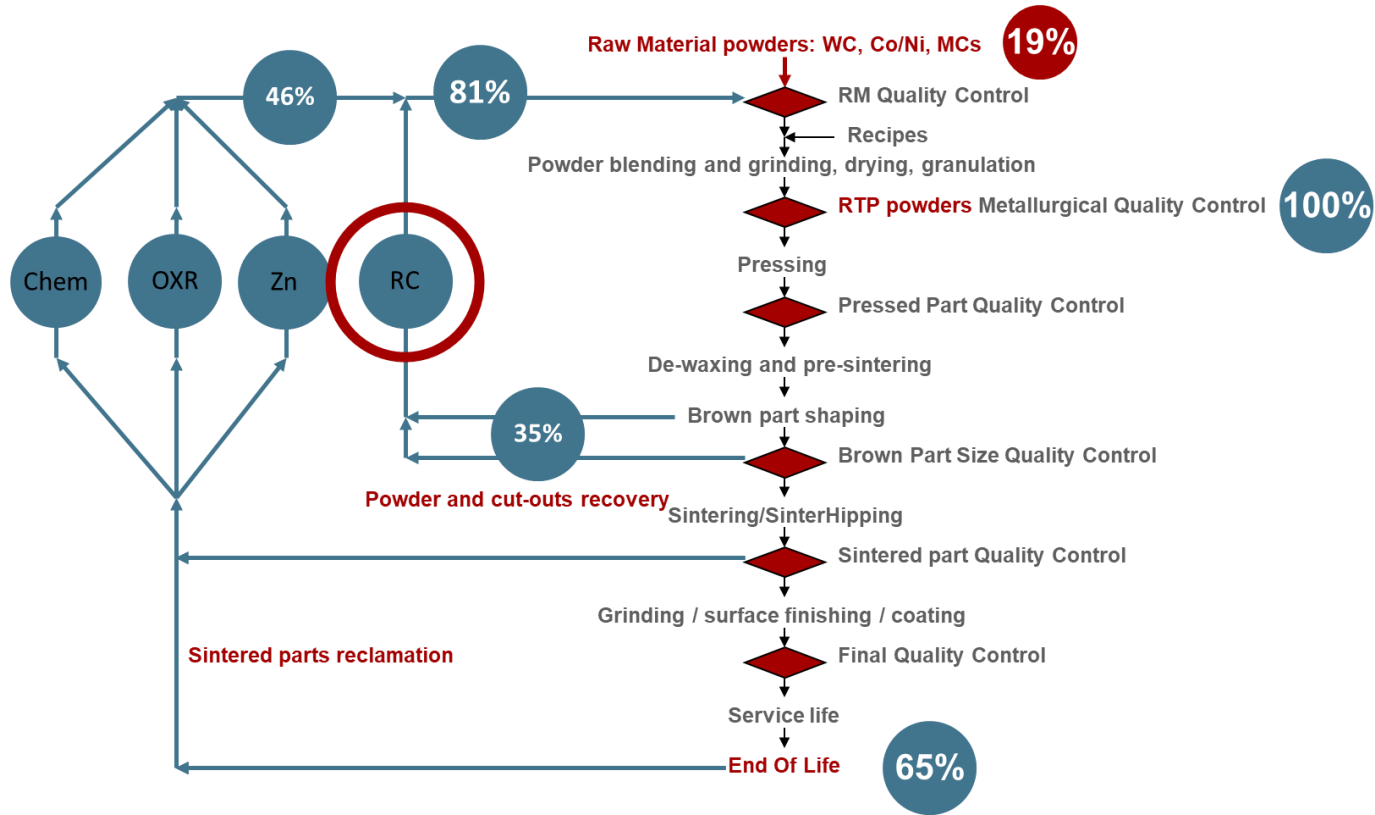
Substitutability index: >0.7

Co price volatility



Substitutability index: 0.7

HM: Life Cycle and the OMCD recycling model



HM recycling: the RC powder

Collection procedures:

- ✓ Pure grades
- ✓ Mixed powders



9 different RC-types

Parameters for the definition of **RC types**:

Chemical composition:

- ✓ γ -phase (Ti, Ta, Nb, Zr)
- ✓ metallic binder (Co vs. Ni)

WC grain size:

- ✓ ultrafine
- ✓ small-fine
- ✓ medium
- ✓ coarse

Chemical composition, by:

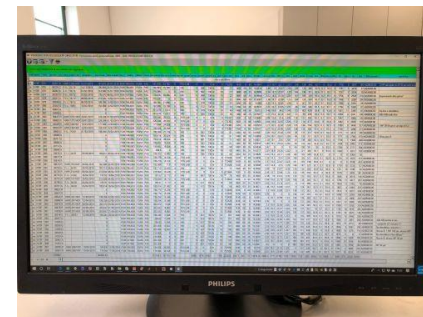
- ✓ ICP-OES (trace elements)
- ✓ IRS (carbon and oxygen)

Physical-metallurgical characterization:

- ✓ density
- ✓ hardness (HRA, HV)
- ✓ Transverse Rupture Strength (TRS)
- ✓ magnetic moment at saturation
- ✓ coercive force
- ✓ optical microscopy (100x, 200x, 1500x)



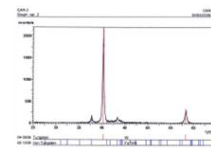
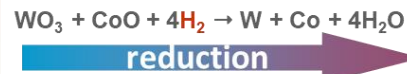
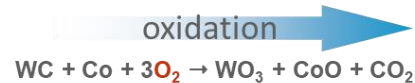
extractor fan & filters



OXR process

Pilling-Bedworth ratio R_{PB} :

$$R_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide}}{\rho_{oxide}} \frac{\rho_{metal}}{n \cdot M_{metal}}$$



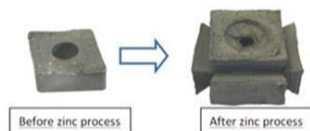
HM recycling: the Zinc process

- ✓ Molten zinc forms an alloy system with cobalt (at $T \leq 900$ °C under Ar pressure):
 CoZn_{13} (γ_2)

- ✓ Lattice parameters ratio Co vs. $\text{CoZn}_{13} \approx 2.5 \div 3$



Hardmetal scrap is destroyed

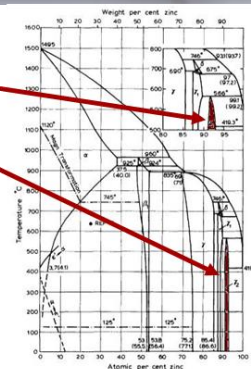


source: Tikomet Oy, <https://www.tikomet.fi/en/recycling-hardmetal/>

- ✓ Zn is distilled under vacuum at $T \geq 800$ °C and condensated for recovering. Co attached to WC particles



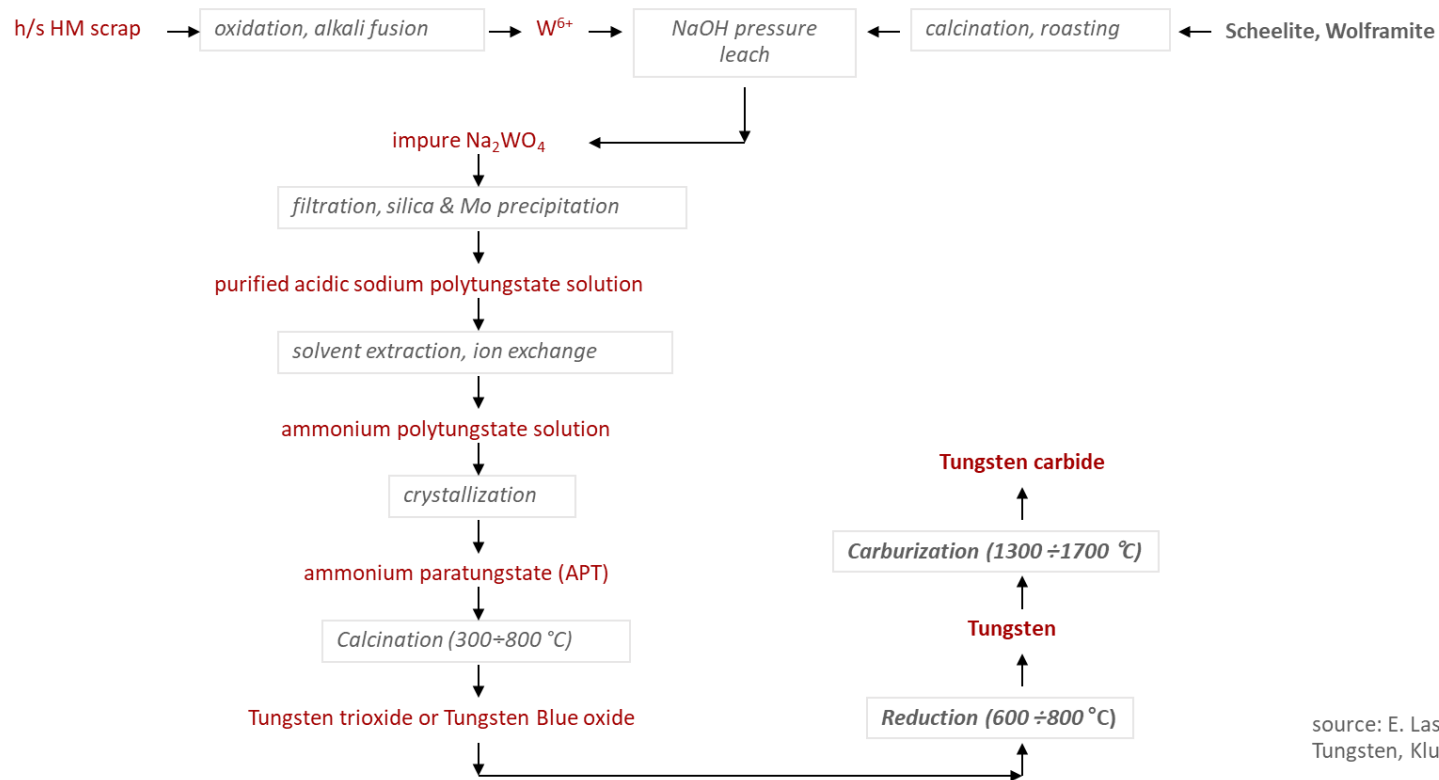
- ✓ Destroyed scrap is crushed and sieved, in order to obtain powder



H. Comert, J.N. Pratt, The thermodynamic properties of solid Cobalt-Zinc alloys, Thermochimica Acta 59 (1982) 267-285

HM recycling: the Chemical Conversion

Hard/soft scraps are treated together with ore in the **modern Tungsten Hydrometallurgical Process**



source: E. Lassner, W.-D. Schubert, Tungsten, Kluwer Academic (1999)

HM recycling: the Chemical Conversion



SERICHIM is a R&D company founded in 2006 as a spin-off of the Research and Development Center of a major Italian chemical company.

Located in Torviscosa (UD), **SERICHIM** employs 21 highly prepared scientists with extensive research and industrial experience.

HM recycling: the Chemical Conversion

SERVICES OFFERED:

PRODUCT DEVELOPMENT: studies of synthetic pathways and preparation of chemicals and API from few grams to hundred kilos for Fine Chemical and Pharmaceuticals company.

PROCESS DEVELOPMENT: measure and collection of data required for process development, with simulation of unit operations and experimental check of their performances until the pilot scale

CIRCULAR ECONOMY: studies of technological solutions to favor the replacement of virgin raw materials with materials coming from recovery chains that preserve their qualities (secondary raw materials) by a sustainable chemistry.

... moving beyond the state of the art

HM recycling: the Chemical Conversion

FILMS REQUEST:

To carry out a study for the recovery of Tungsten (W) and Cobalt (Co) from hard-metal scraps (WC-Co) after air oxidation at 850 °C



HM recycling: the Chemical Conversion

SERICHIM PROPOSALS:

Hydrometallurgical treatment by:

a) Alkali leaching of WO_3 (followed by acid precipitation of tungstic acid)

or

b) Acid leaching of CoO

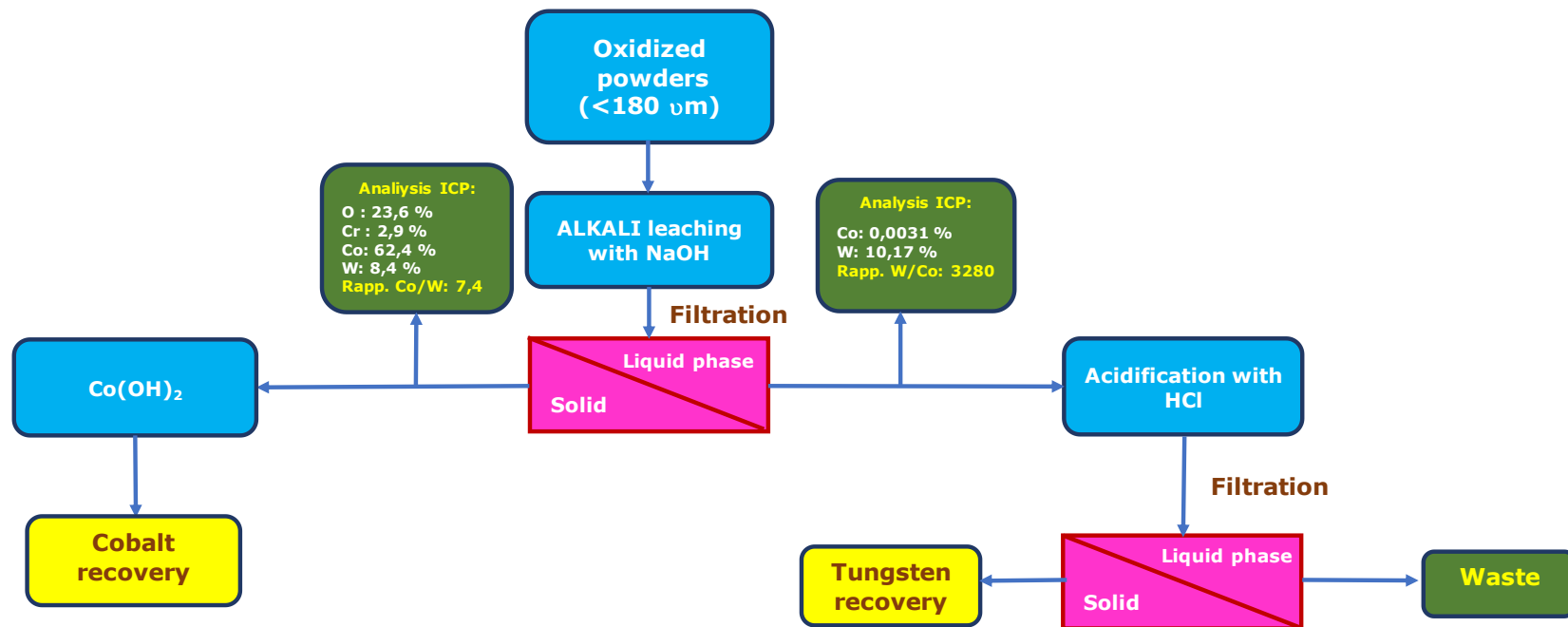
HM recycling: the Chemical Conversion

ALKALI LEACHING of WC-Co oxidized powders



HM recycling: the Chemical Conversion

ALKALI LEACHING of WC-Co oxidized powders



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HM recycling: the Chemical Conversion

ALKALI LEACHING of WC-Co oxidized powders



**Oxidised powder
slurry alkali treated
at $t=0$**



**Oxidised powder
slurry at end reaction**



**Na_2WO_4 solution
after filtration**

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HM recycling: the Chemical Conversion

ALKALI LEACHING of WC-Co oxidized powders



**Wet Co(OH)_2
after filtration**



**Solid Co(OH)_2
after drying**

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HM recycling: the Chemical Conversion

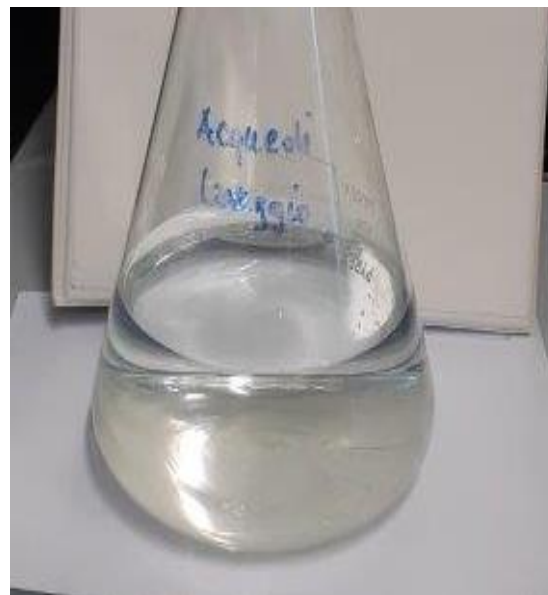
ALKALI LEACHING of WC-Co oxidized powders



**Na₂WO₄ solution
after acidification
with HCl**



H₂WO₄ dried



**Mother liquor
after filtration**

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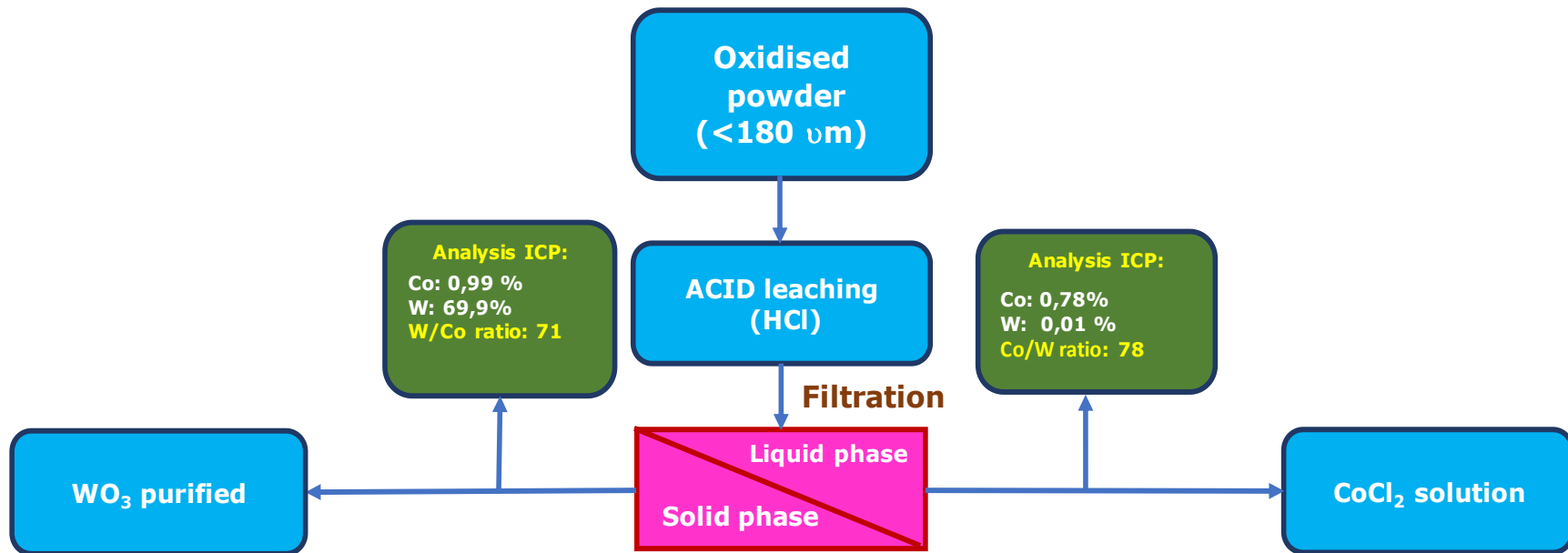
HM recycling: the Chemical Conversion

ACID LEACHING of WC-Co oxidized powders



HM recycling: the Chemical Conversion

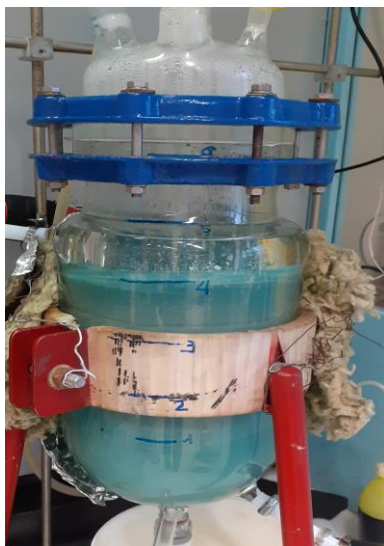
ACID LEACHING of WC-Co oxidized powders



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HM recycling: the Chemical Conversion

ACID LEACHING of WC-Co oxidized powders



**Oxidised powder slurry
acid treated at $t=0$**



**Oxidised powder slurry
during acid leaching**

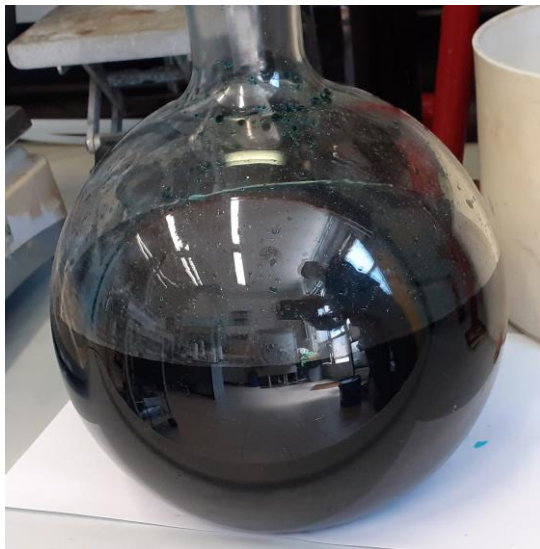


**Oxidised powder
slurry at the end of
acid leaching**

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HM recycling: the Chemical Conversion

ACID LEACHING of WC-Co oxidized powders



**CoCl₂ solution
after filtration**



**Wet WO₃
after filtration**



Dried WO₃

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Conclusions

The effective co-operation between a SME and a private research center is causing:

- (a) the recovery of two strategic elements, as tungsten and cobalt, that have been listed as Critical Raw Materials by EU, helping both EU and Italy to keep the status of industrial economies and developing the high potential of «city mining»
- (b) a crucial step forward on the way of the OMCD Group to reach independency in the raw material supply, in a context where most of the HM competitors have acquired traditional WC powders suppliers.
- (c) building up and spreading of knowledge and practice of the chemistry of relevant metallic elements.

HM recycling: the Chemical Conversion

Grazie per l'attenzione



.... moving beyond the state of the art