Critical Minerals (..er Penalty Elements) from Mine to Metal in the Copper Supply Chain

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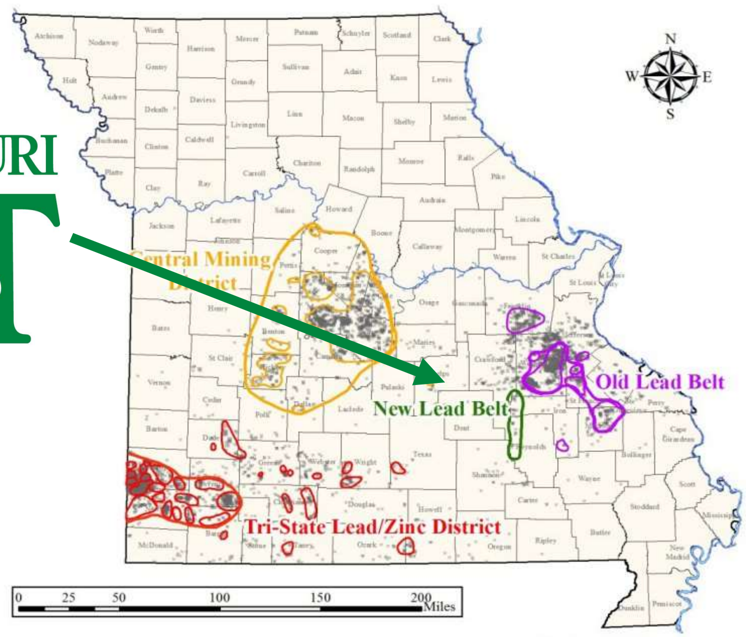
O'KEEFE INSTITUTE SUSTAINABLE SUPPLY OF STRATEGIC MINERALS

MISSOURI S&T

Missouri S&T

- Missouri University of Science and Technology
  - Known as University of Missouri-Rolla (UMR) 1962-2007
  - Missouri School of Mines and Metallurgy 1870-1962
- Enrollment
  - ~7650 total students (6100 undergrads and 1550 grads)
  - >90% majoring in STEM
- Programs covering entire metal supply chain
- Research
  - $35-40 million per annum



Thomas J. O'Keefe Institute for the Sustainable Supply of Strategic Minerals

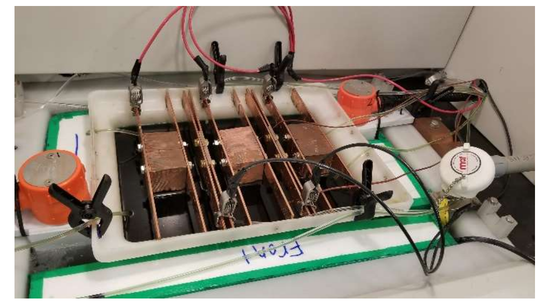
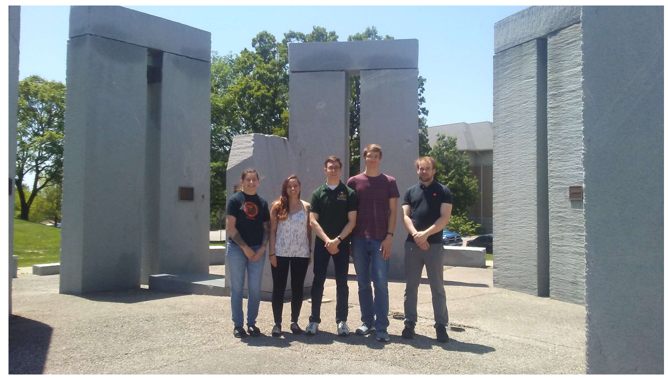
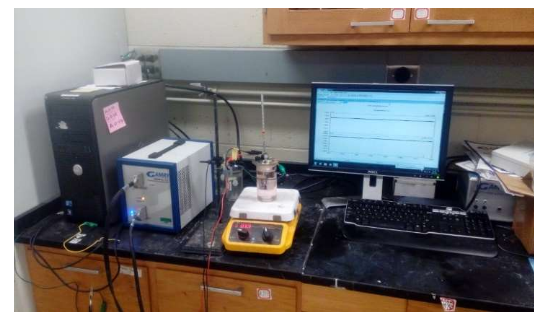
O'KEEFE INSTITUTE SUSTAINABLE SUPPLY OF STRATEGIC MINERALS

- Combining existing excellence at Missouri S&T to develop technology, methodologies and policy to facilitate sustainable supply of strategic minerals for United States
- Member of the Critical Materials Institute

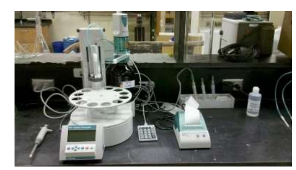
mining.mst.edu/research/okeefe-institute/

- Aqueous and Electrolytic Processing of Metals
  - Critical Minerals
    - Battery grade Co production from Missouri resources
    - Ga, Ge, In capture from domestic zinc processing
  - Copper Electrowinning
    - Amira P705D – base metal electrowinning
  - Copper Electrorefining
    - Group 15 elements deportment
    - Impact of nickel on cathode
  - Electrogalvanizing
    - Improving zincate plating operation
  - Grinding Media Corrosion

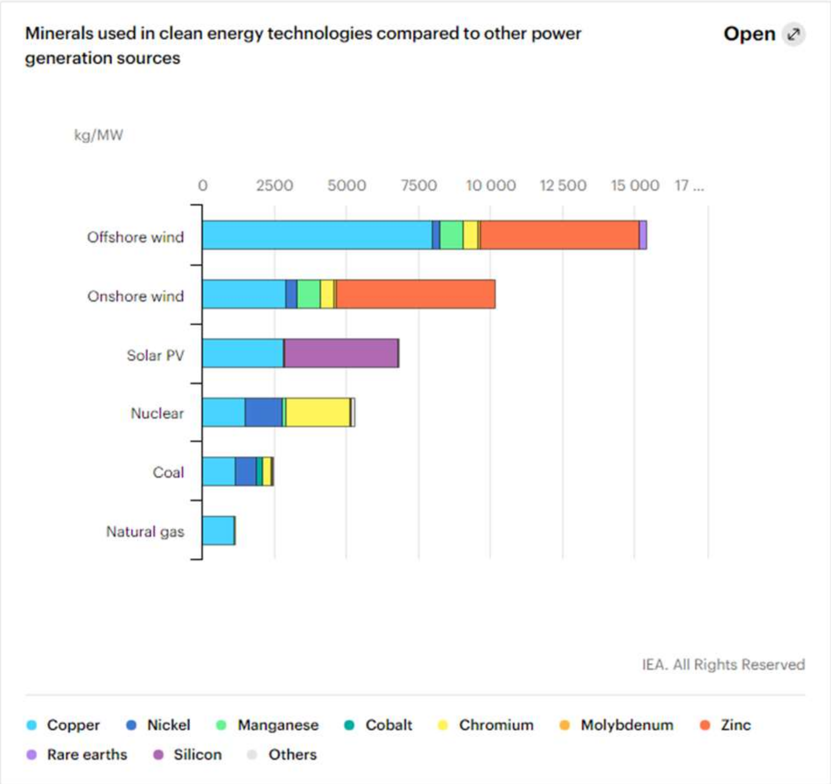







Decarbonization = Metal Production



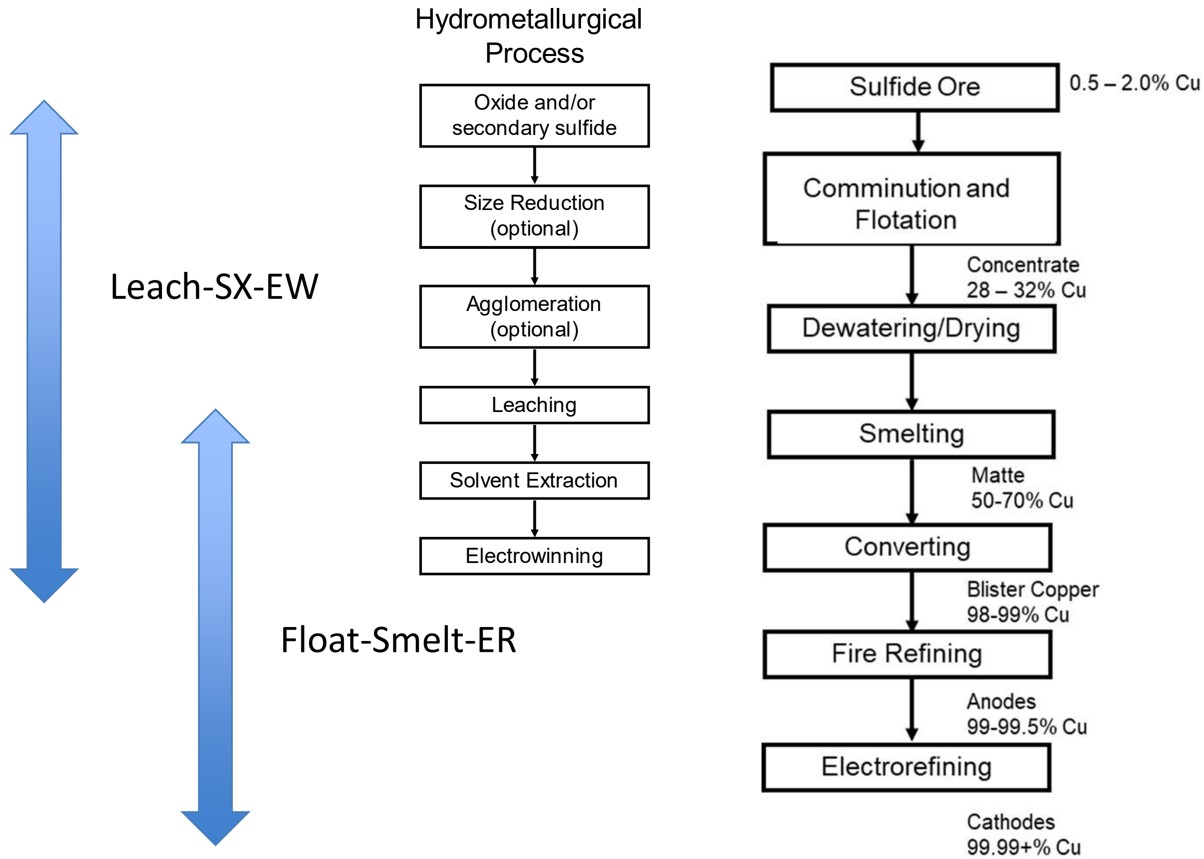
- "Concerns about resources relate to quality rather than quantity."
- Long term trend – ore grades are declining; deposits are becoming more complex (more impurities)

IEA (2021), The Role of Critical Minerals in Clean Energy Transitions, IEA, Paris https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions

Primary Copper Process Determined by Mineralogy

By-products mostly from non-hydrometallurgical processing

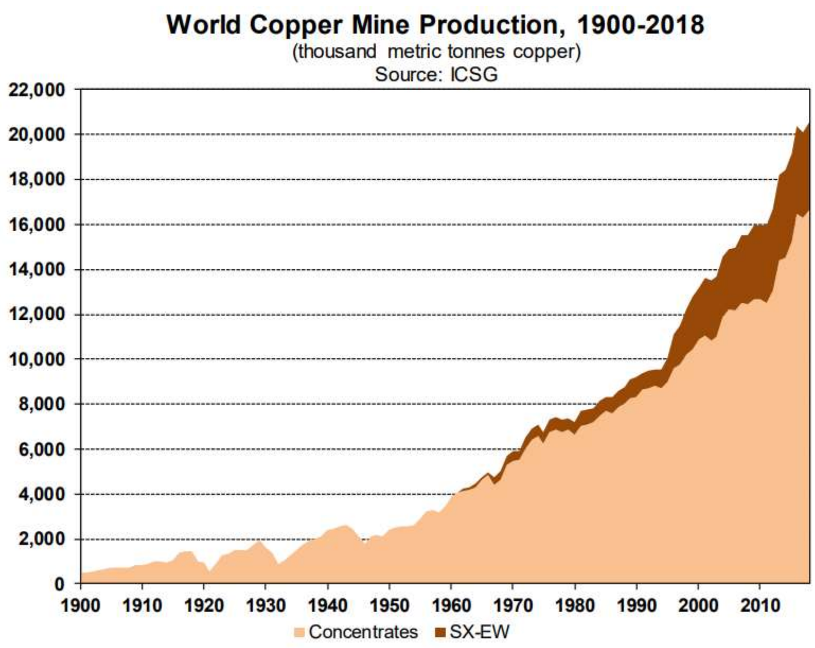
- "Oxides"
  - Malachite
  - Chrysocolla
  - Atacamite
- Secondary Sulfides
  - Covellite
  - Chalcocite
- Primary Sulfide
  - Chalcopyrite

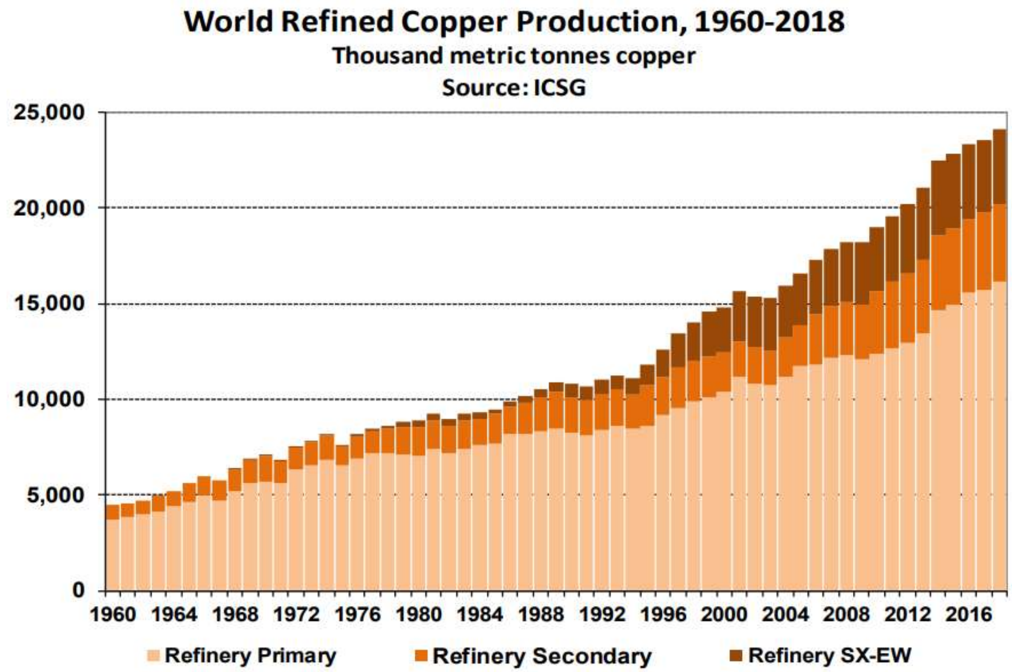


Copper Production

Concentrate Growth Faster than SX-EW

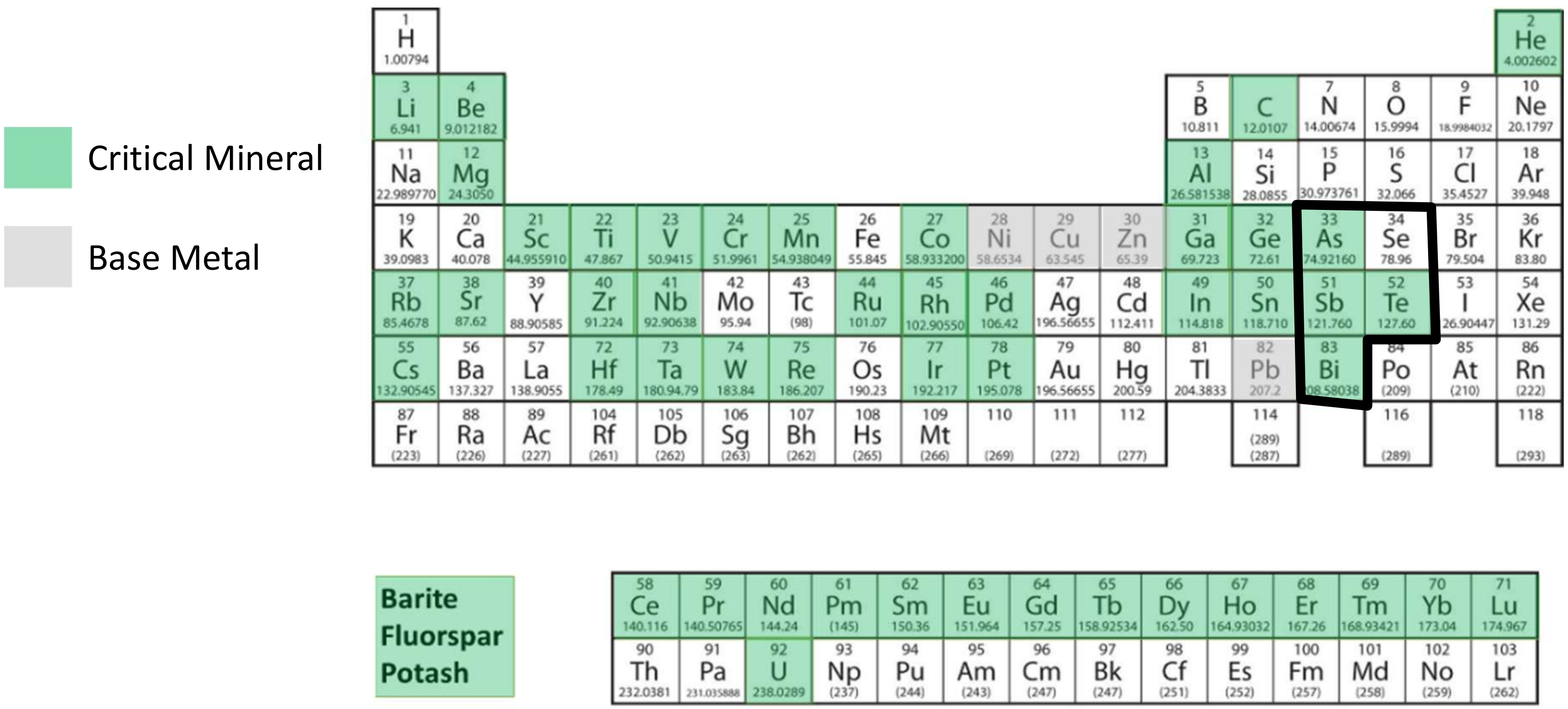
World: Primary Refinery ~ 66%, Secondary Refining ~ 17%, SX-EW ~17%





https://www.icsg.org/index.php/component/jdownloads/finish/170/2965

2017 USGS Critical Minerals List



Energy Minerals

Batteries
Li, Co, Ni, Mn
Pb, Sn, Sb

Solar
Te, Si

Wind
REE, Co, Sc

Infrastructure
Cu, Fe, Al, Ag, Au

Some Critical Minerals are Penalty Elements

ASTM B115-00 Copper Specification

Element	Grade 1
Copper	99.95% min
Selenium, max	2 ppm
Tellurium, max	2 ppm
Bismuth, max	1.0 ppm
Group total, max	3 ppm
Antimony, max	4 ppm
Arsenic, max	5 ppm

- As, Sb, Bi are penalty elements in the concentrate
- Smelters charge miners for their presence above contractual levels
  - It costs money to dispose of the elements
  - The elements can foul the process and produce off spec copper

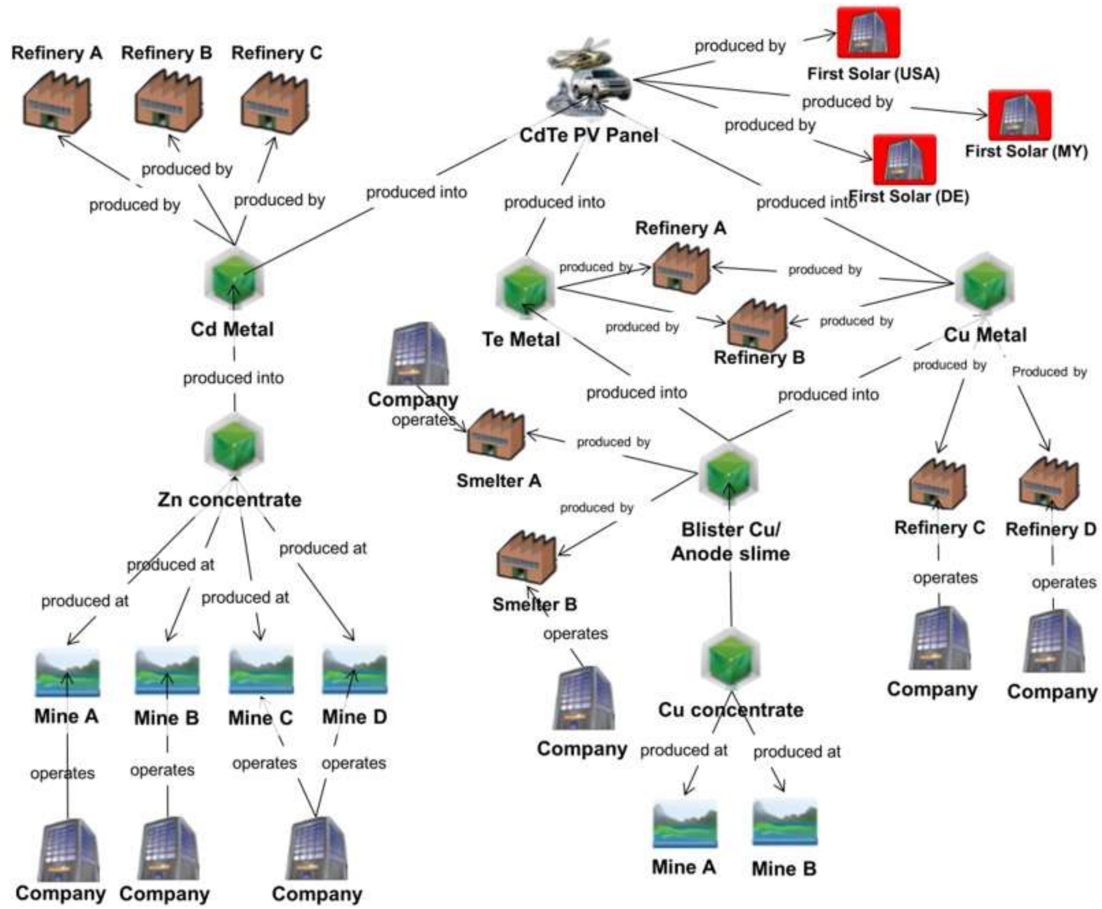
Table 1 – Japanese copper smelter penalty elements

Element	Charge (US$/t)	For each (%)	Exceeding (%)
As	2.50	0.1	0.2
Sb	0.50	0.01	0.1
Bi	0.30	0.01	0.05
Cl	0.50	0.01	0.05
Pb	1.50	1.0	1.0
Zn	1.50	1.0	3.0
Ni + Co	0.30	0.1	0.5
Al_2O_3 + MgO	4.50	1.0	5.0
F	0.10	10 ppm	330 ppm
Hg	0.20	1 ppm	10 ppm

Fountain, C., 2013. The whys and wherefores of penalty elements in copper concentrates, in: MetPlant 2013. Australasian Institute of Mining and Metallurgy, pp. 502–518.

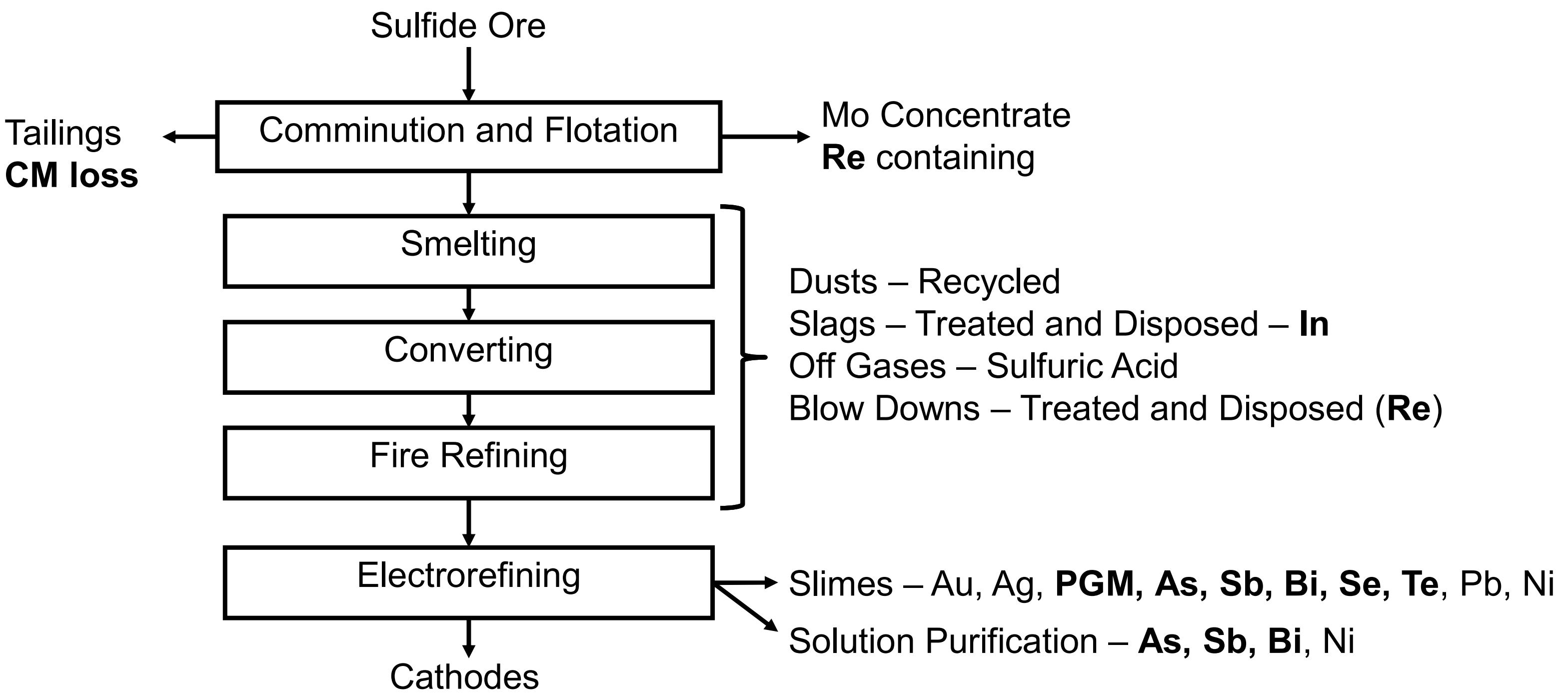
Can We Create Value from Impurities?

- Can we create silk purses out of sow ears?



Nuss, P., T. E. Graedel, E. Alonso, and A. Carroll. "Mapping supply chain risk by network analysis of product platforms." Sustainable Materials and Technologies 10 (2016): 14-22.

Critical Minerals in Float-Smelt-Refine Process



In North America, copper hydrometallurgical process does not produce by-products

CM in Copper Deposits

- Porphyry deposits
  - Large-to-giant in size
  - Low-to-medium Cu grade
  - ~ 60 - 95% of global copper supply
- Deposits can host 10s to 100s ppm of critical elements
  - Commonly concentrated within sulfide minerals
    - Pyrite, Chalcopyrite, Bornite
  - Se and Te substitute for sulfur or tellurides
  - As and Sb in complex Cu sulfide minerals
  - Bi in complex or simple sulfides
- Generally, lack of information on the distribution behavior of critical elements within orebodies
  - Inaccurate sampling and assaying due to huge volumes and low grades
  - Potential association with gold and/or PGMs?

Maximum reported concentrations (ppm) of critical elements in chalcopyrite, bornite and pyrite from porphyry and other deposits

Mineral	Deposit Type	Se	Te	As	Sb	Bi
Chalcopyrite ($CuFeS_2$)	Porphyry	300	300	500	1000	0.53
	Skarn	538	6.6	0.54	0.28	37.9
	Epithermal	300	0.04	0.73	4.2	0.05
Bornite (Cu_5FeS_4)	Porphyry	277	27.4	-	0.01	424
	Skarn	1046	148	2.3	44	7666
	Epithermal	299	75	8.1	11	839
Pyrite (FeS2)	Porphyry	5.46	26.3	3230	-	-
	Epithermal	535	343	2086	-	-
	Carlin	4284	6600	472200	-	-
	Orogenic	199	20823	474000	-	-

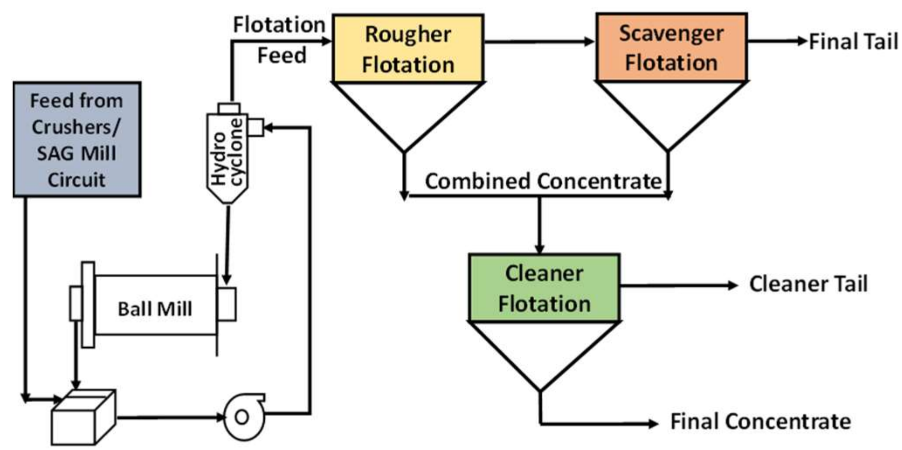
Moats, M., Alagha, L., & Awuah-Offei, K. (2021). Towards resilient and sustainable supply of critical elements from the copper supply chain: A review. Journal of Cleaner Production, 127207.

Deportment during Mineral Processing

Concentrations of Se, Te, As, Sb and Bi in copper sulfide concentrates from different plants

Element	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Cu (%)	21.7	16-19	25-28	20-26	41-45	28-32	16.6	-	-	-
Se(ppm)	-	8-15	<100	-	23	16	124	58	62	139
Te(ppm)	-	5-8	<100	<50	4.2	1.6	n/a	10	4.9	12
As(ppm)	3400	-	<100	<200	10	10	1197	-	-	-
Sb(ppm)	1600	-	<100	<100	5	7	8	-	-	-
Bi(ppm)	-	-	-	-	-	-	648	250	270	16

C1: Boliden/Sweden; C2:Hindustan Khetri./India; C3: Hindustan M Malanjkhand/India; C4: Assarel-Medet/Bulgaria; C5: Lumwana Malundwe/Zambia; C6: Lumwana Chimiwungo/Zambia; C7: Copper concentrator North America; C8: Mission Mine Complex-North/AZ-USA; C9: Mission Mine Complex South/AZ-USA; C10: Ray Mine/ AZ-USA



- Lack of information during rougher and scavenger stages of flotation
- Current public data are incomplete or inconsistent
  - Simple mass balance calculations
  - Lack of associated mineralogy for CMs
  - Poor fundamental understanding of CM deportment

- Two studies have examined Te deportment
  - ~10% Te reports to concentrate

Moats, M., Alagha, L., & Awuah-Offei, K. (2021). Towards resilient and sustainable supply of critical elements from the copper supply chain: A review. Journal of Cleaner Production, 127207.

Smelting and Converting

- Depends on furnace type
  - Most smelters recycle their dust (off gases)
  - Critical minerals eventually deport to anode or slag
- Difficult data to obtain
  - Values reflect grab samples
  - Confidential/proprietary information for custom smelters

Smelting

Furnace	Arsenic (%)			Antimony (%)			Bismuth (%)		
	Matte	Slag	Gas	Matte	Slag	Gas	Matte	Slag	Gas
Outotec Flash	15-40	5-25	35-80	60-70	5-35	5-25	30-75	2-30	15-65
ISASMELT	5-9	3-18	73-90	19-40	3-52	8-72	4-24	0-1	75-96
SKS	6	12	82	12	71	17	19	11	70

Furnace	Selenium (wt%)			Tellurium (wt%)		
	Matte	Slag	Gas	Matte	Slag	Gas
Outotec Flash	85	5-15	0-5	60-91	7-30	2-15
ISASMELT	n.d.	n.d.	n.d	71	18	11

Converting

Furnace	Arsenic (wt%)			Antimony (wt%)			Bismuth (wt%)		
	Blister	Slag	Gas	Blister	Slag	Gas	Blister	Slag	Gas
Pierce-Smith	10-60	0-62	12-92	4-78	7-89	9-50	13-75	2-30	15-67
Flash	42-52	28-42	6-32	n.d	n.d.	n.d	65-73	14-16	13-21

Furnace	Selenium (wt%)			Tellurium (wt%)		
	Blister	Slag	Gas	Blister	Slag	Gas
Pierce-Smith	70-72	5-6	21-25	42	n.d.	58

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Flue Dust

Description	Cu(%)	Se(%)	Te(%)	As(%)	Sb(%)	Bi(%)
"Flue Dust"	6-30	<0.01	0.2	1-20	0.03-3	0.01-3.5
Outotec Flash	11-30	0.04	0.01	0.9-9	0.01-0.9	0.11-0.6
Bottom Blowing	15-28	n.d.	n.d.	8-14	n.d.	0.7-1.7
Pierce-Smith Converter	3.9-5.5	n.d.	n.d.	2.8-7.7	0.12-3.1	1.2-3.2

- Calculated ~1.2 million tonnes of dust per annum generated during copper smelting
- Dust recycling within a smelter increases concentrations of CM
  - Not clear what the sustainable production potential of these elements would be
  - Te concentration is from one published value

Value of potential critical elements in smelter flue dusts. Prices reflect average 2015-2019 price for Cu, Se, Te, Sb and Bi metals and As_2O_3 (USGS, 2020)

Potential in Flue Dusts	Cu	Se	Te	As	Sb	Bi
Dust Grade	18%	0.005%	0.2%	10%	1.5%	1.8%
Price (USD/kg)	5.8	42	134	0.58	8.1	10.6
Tons per year contained in dust	216000	60	2400	120000	18000	21600
Value (millions USD/yr)	1300	3	320	60	150	230
% of total value in flue dusts across these elements	62.1	0.1	15.9	3.3	7.2	11.3

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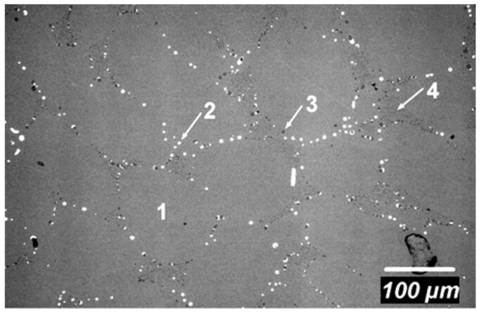
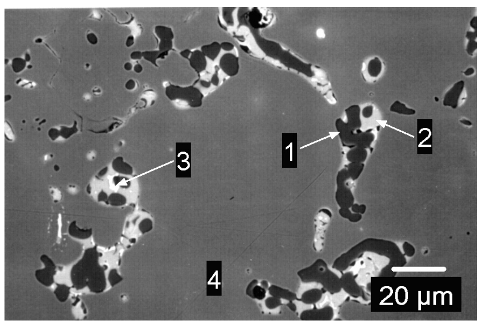
Electrorefining Anodes

Element	Weighted Average Anode Composition (ppm)
Selenium	390
Tellurium	113
Arsenic	1239
Antimony	323
Bismuth	257

M. Moats, L. Alagha, and K. Awuah-Offei. Towards resilient and sustainable supply of critical elements from the copper supply chain: A review. Accepted by *Journal of Cleaner Production*

Deportment of Critical Minerals in Electrorefining





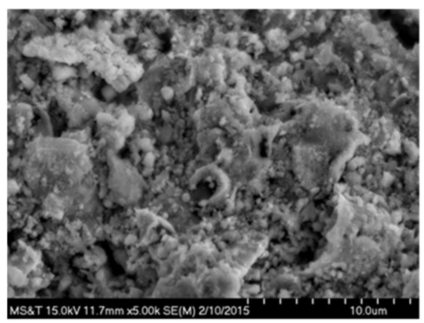
Element	Anode		After Dissolution	
	Solid Solution	Inclusion	Slimes	Electrolyte
Selenium	0%	100%	98%	2%
Tellurium	0%	100%	98%	2%
Arsenic	30-60%	40-70%	20-80%	20-80%
Antimony	10-30%	70-90%	30-70%	30-70%
Bismuth	0%	100%	30-70%	30-70%

M. Moats, L. Alagha, and K. Awuah-Offei. Towards resilient and sustainable supply of critical elements from the copper supply chain: A review. Under review by *Journal of Cleaner Production*

Slimes

Characteristics		Average Value	
kg per tonne of anode		5.5	
Element	%	Element	%
Cu	21.7	As	3.3
Ag	9.4	Sb	3.9
Au	0.7	Bi	1.3
S	5.5	Pb	11.6
Se	8.3	Fe	0.2
Te	1.9	Ni	3.8

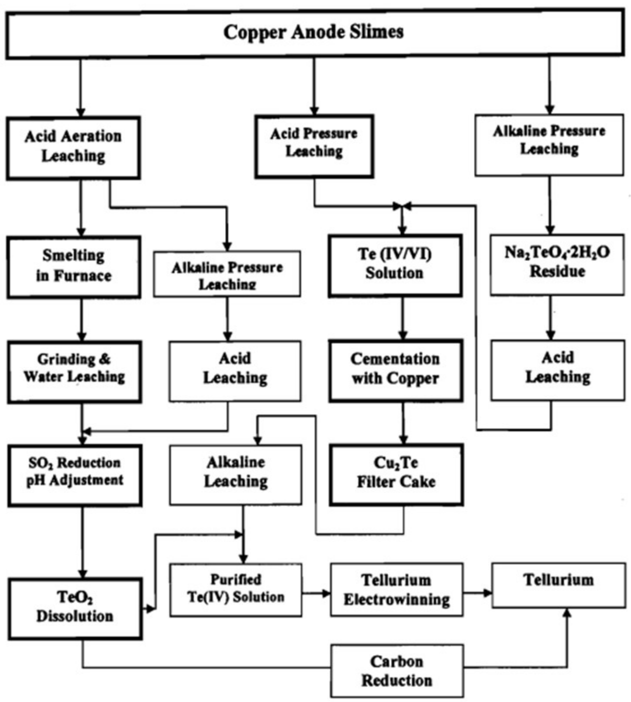
M. Moats, A. Filzwieser, S. Wang, W. Davenport, T. Robinson, A. Siegmund (2019) Global Survey of Copper Electrorefining: 2019 World Tankhouse Operating Data. Proceedings of the 58th Annual Conference of Metallurgists (COM) hosting the 10th International Copper Conference – Copper 2019, Vancouver, Canada, August 18-21, 2019



- Significant enrichment of Se, Te, As, Sb and Bi
- Facilities the potential recovery of critical minerals while targeting the recovery of gold and silver

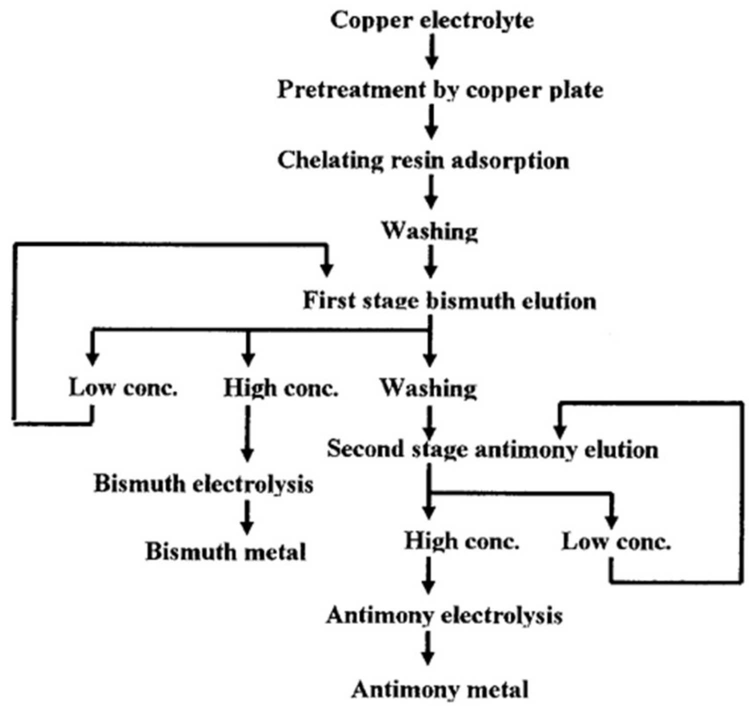
Critical Mineral Recovery – Many Options

Industrial



Wang, S., Westrom, B., & Fernandez, J. A. (2003). The recovery of tellurium from copper refinery slimes. COBRE 2003 Volume V, 273-285.

Developmental



Ando, K., & Tsuchida, N. (1997). Recovering Bi and Sb from electrolyte in copper electrorefining. *JOM*, *49*(12), 49-51.

2014-2019 World Survey Data Analysis
By-Product Potential in Anodes

31 Refineries Surveyed – 8.0 million tonnes of Refined Copper (40% of World Production)

Element	Calculated world potential in anodes, t/yr	Estimated 2019 world production, t
Selenium	7900	2800
Tellurium	2300	470
Arsenic	25000	25000
Antimony	6500	160000
Bismuth	5200	19000

Potential value (millions USD/yr) of metals contained in copper anodes at U.S. refineries

Element	Refinery 1	Refinery 2	Refinery 3	Price
Copper	1200	800	1200	$5.8/kg
Gold	290	12	68	$1270/tr.oz.
Silver	47	49	74	$16.4/tr.oz.
Selenium	5.3	3.0	5.1	$42/kg
Tellurium	2.3	1.1	1.5	$134/kg
Arsenic	0.22	0.03	0.04	$0.55/kg
Antimony	0.05	0.09	0.29	$8.1/kg
Bismuth	1.2	0.26	0.24	$10.6/kg

2019 Production and Import data from USGS - https://www.usgs.gov/centers/nmic/commodity-statistics-and-information

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https://www.riotinto.com/en/news/releases/2021/Rio-Tinto-to-build-new-tellurium-plant-at-Kennecott-mine

North America Copper Refineries Critical Minerals

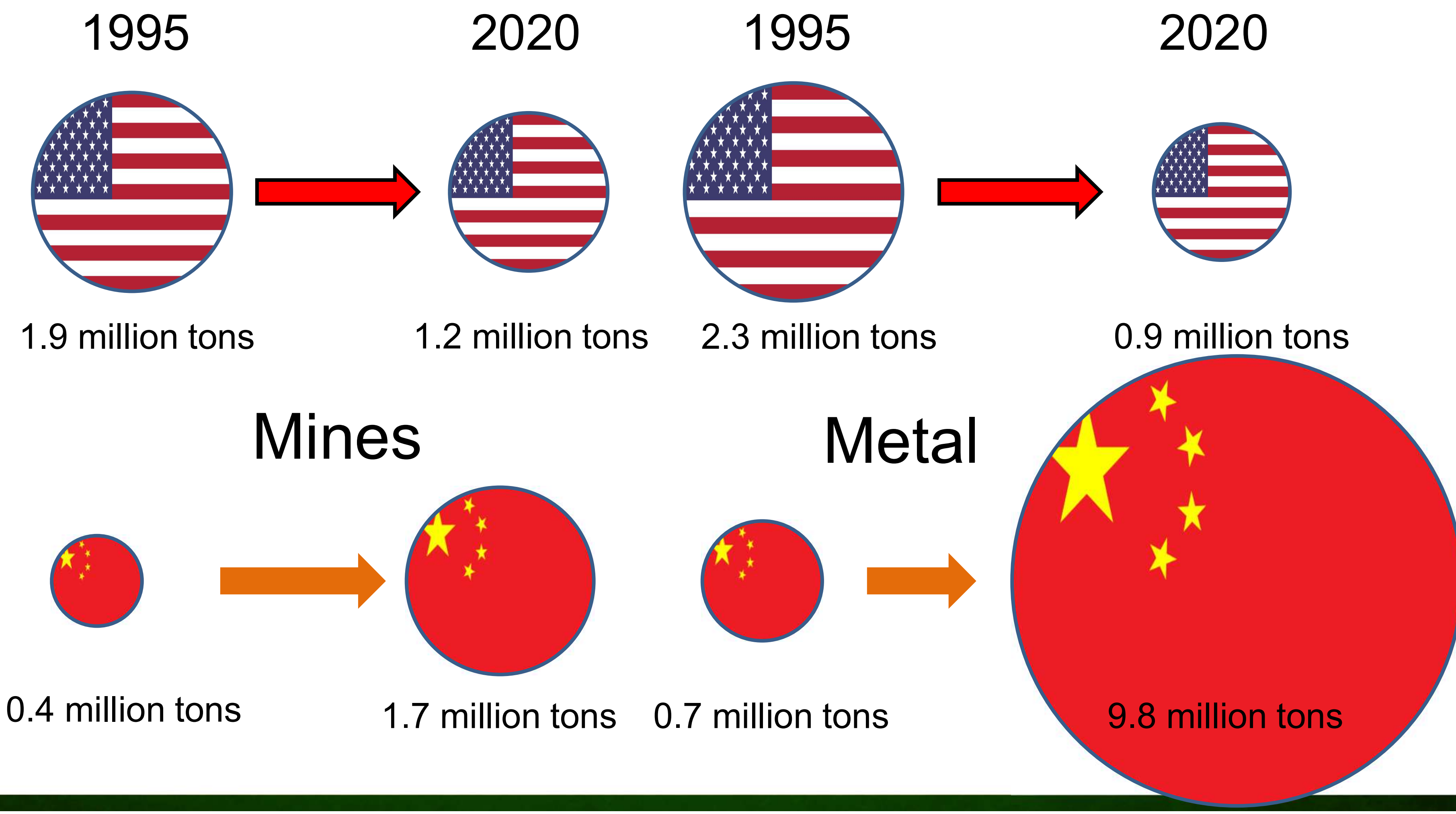
- Refinery 1
  - Extracts Sb and Bi from electrolyte – disposed
  - Se and Te recovery (processes other refineries Cu_2Te)
  - PGM recovery
  - Sb, Bi, As recycled to smelter
- Refinery 2
  - Treats slimes from two refineries
  - Te and Se recovery
  - PGM recovery
  - Bleeds solution to SX – Te, Sb, Bi loss
- Refinery 3 (on care and maintenance)
  - Te recovery as Cu_2Te
  - Se recovery circuit – not running
  - PGM recovery – not running
  - Slimes further processed elsewhere
  - Bi recovery circuit with salable product – not running
  - Sb, Bi, As in solution disposed
- Refinery 4
  - Te recovered as Cu_2Te
  - Slimes processed elsewhere
  - Sb, Bi, As recycled to smelter
- Refinery 5
  - Te recovered as Cu_2Te (being built)
  - Se recovered
  - Bi recovery pilot designed, but not built, disposed
  - Sb, As are disposed

- **Au, Ag and PGM are very valuable and are the focus of recovery**

- **All other elements are impurities and need removal**
  - **Removal may mean recovery, may not**

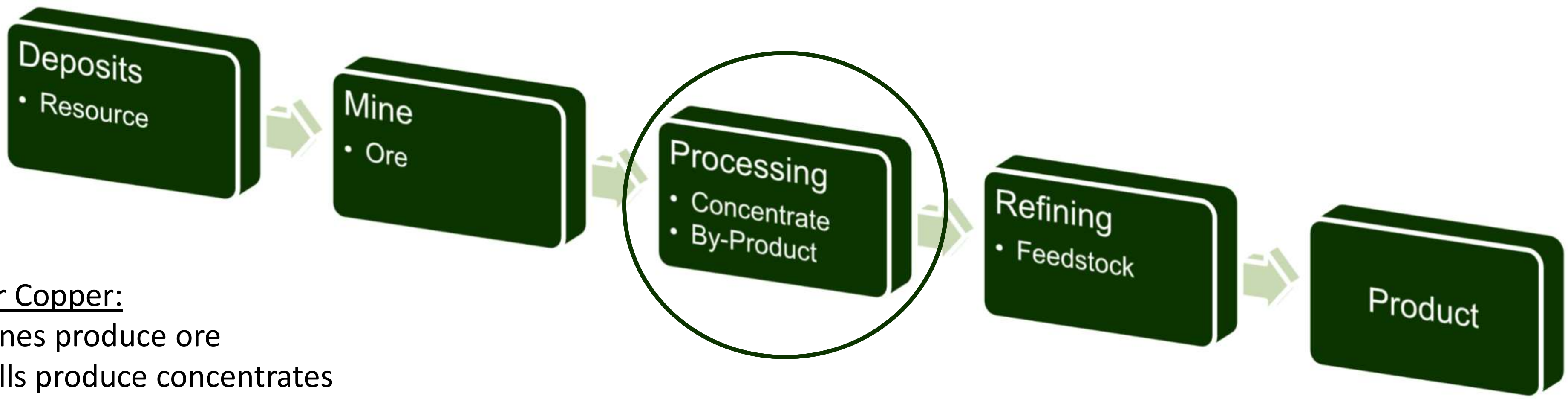
- **Can more Te be recovered?**
- **Can Bi/Sb recovery be targeted?**

Changes in Copper Supply Chain



Critical Minerals By-Products from Metal Production

Just Developing New Mines will not Close the Supply Gap!



<u>For Copper:</u>
Mines produce ore
Mills produce concentrates
Smelters produce anodes
Anodes produce copper and **by-products**
By-products need to be refined separately to produce critical minerals

Closing Domestic Supply Chain Gaps

- **Support mineral exploration to uncover new deposits**
- **Streamline mine permitting process**
- **Develop processing and refining infrastructure and innovation**
- **Facilitate off-take agreements between domestic "mining" and "green energy" companies**
- **Educate workforce needed for critical minerals supply and green energy transition**

Summary

- Primary copper production in North America has declined, so has by-product production
- The world copper supply chain could supply tellurium, bismuth and arsenic needs
  - Without new U.S. smelters, these will be produced elsewhere
- Critical mineral capture suffers because of the relatively low value and low tonnage in the copper supply chain
- Incentives and research are needed to improve critical mineral recovery from the copper supply chain

You are invited!