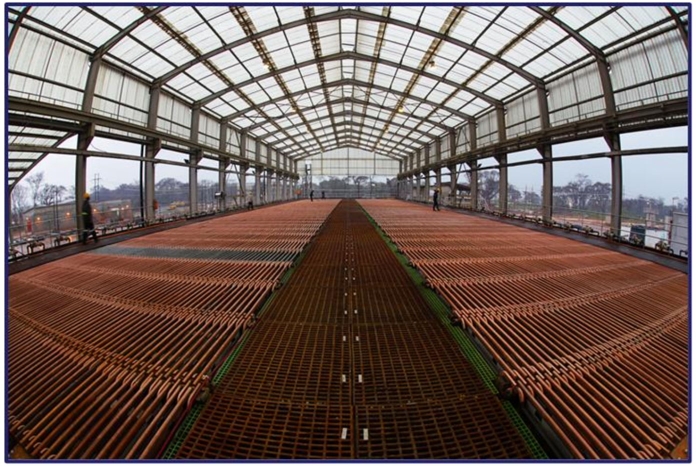
Copper leach–solvent extraction–electrowinning: Keystone technology for sustainable hydrometallurgy



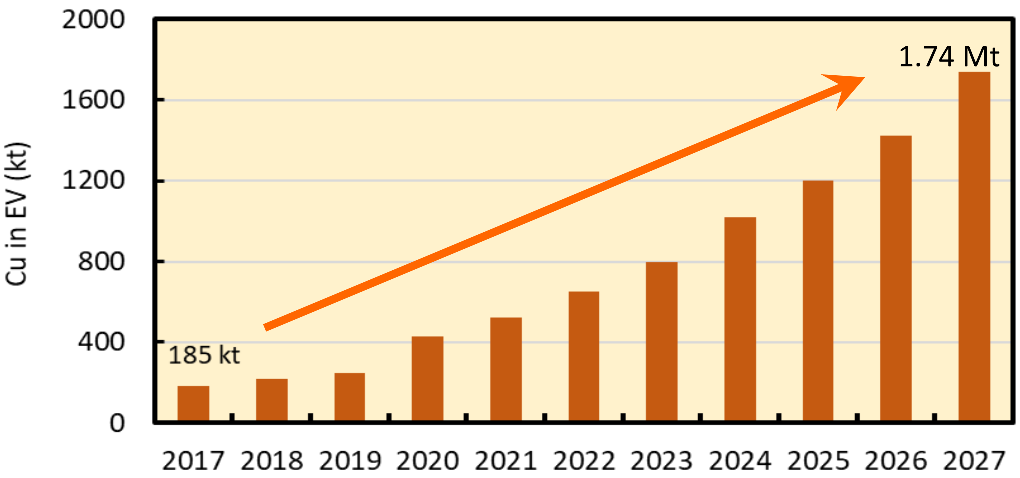
Kathryn C. Sole (PrEng, PhD, FSAIMM, FSAAE)
1st International Circular Hydrometallurgy Symposium
9 September 2024

Copper demand forecast

Electric vehicles

- Electrical grid for charging of EV batteries
- Solar voltaic panels for energy-independent vehicles

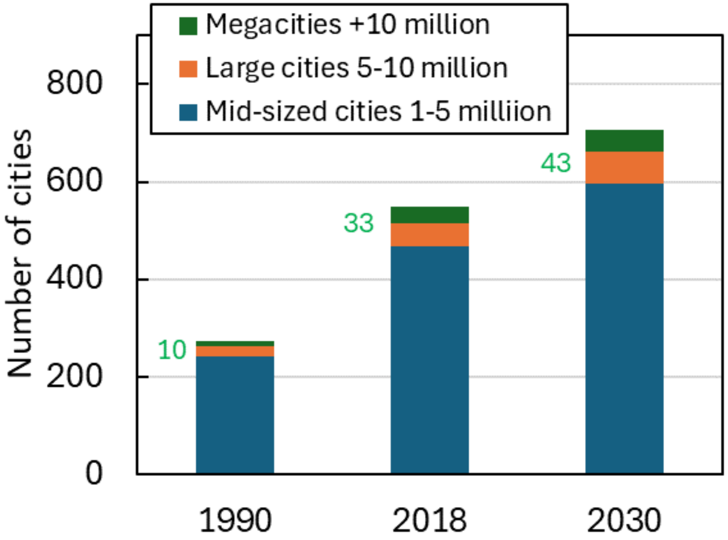
Vehicle	kg Cu
ICE	23
Hybrid EV	40
Plug-in EV	60
Battery EV	83
Hybrid bus	89
Battery bus	220–370



Data from International Copper Study Group (2017)

Copper demand forecast

Urbanisation and megacities



Swann Index - intensity of use of a metal by GDP per capita

Metal	2019 (Mt)	2035 (Mt)	Increase (%)
Nickel	2.4	5.2	116
Steel	1.7	2.6	50
Aluminium	66	103.6	57
Copper	**23.6**	**29.7**	**26**

Driven by decarbonization and the transition to electrification and automated technology

Data from Ghosh (2019), Le Pan (2022)

Process routes for copper ore

1º Sulfides

~ 80%

Concentrating
Smelting
Electrorefining

2º Sulfides / Oxides

~ 20%

Leaching
Solvent extraction
Electrowinning

Cu cathode
> 99.99%

1974: First large-scale copper L-SX-EW

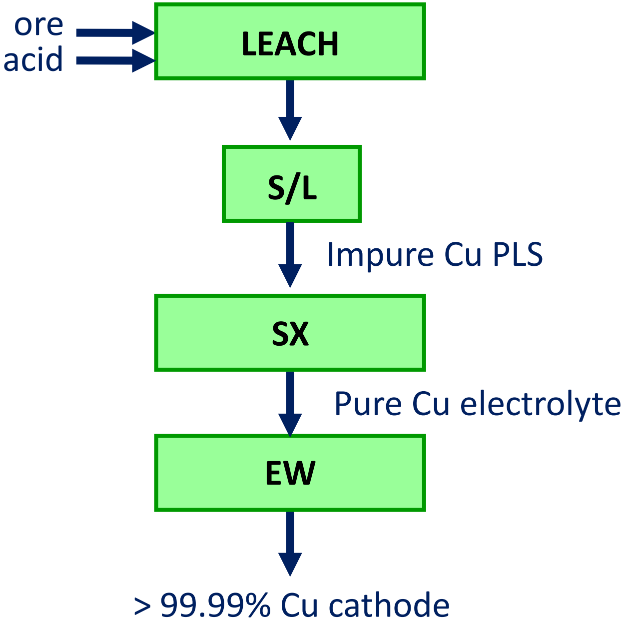
Nchanga Tailings Leach Plant,
Konkola Copper Mines, Zambia

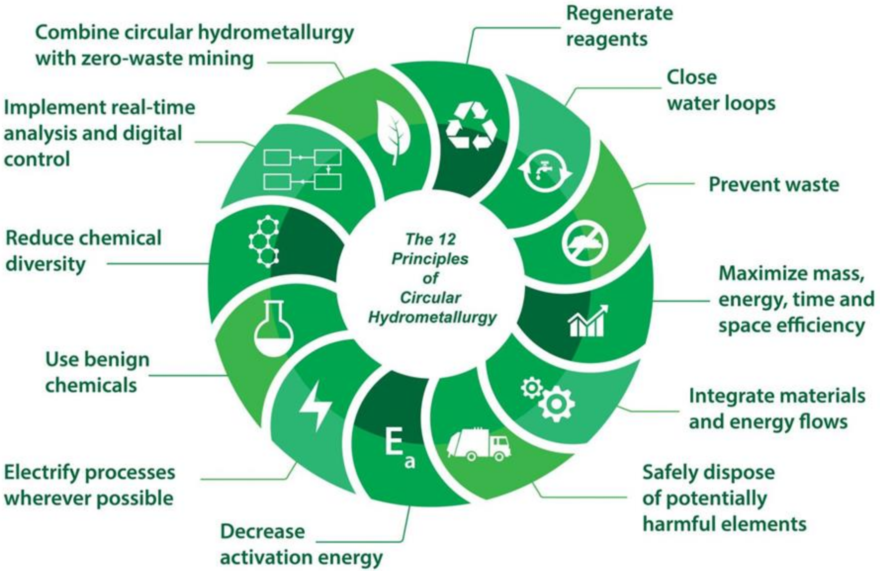
1 Mt/a tailings – 0.4% Cu_{AS} recovered by hydromining
PLS 3 g/L
4 × 3E−2S SX trains

2024:
Still in production
Ramping up to 300 kt/a

Photographs: BASF, Barry Wills, GoogleEarth

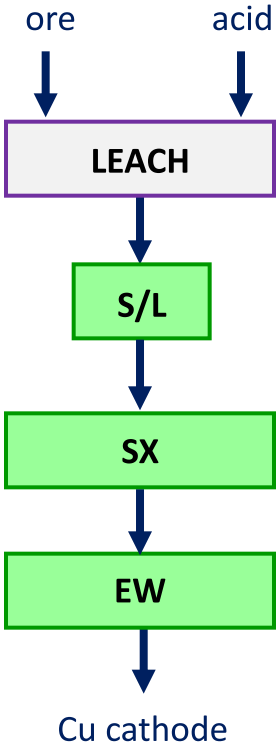
Copper L-SX-EW:
A circular hydrometallurgy flowsheet ahead of it's time





Binnemans & Jones (2023)

Copper L-SX-EW



Oxides

Tenorite: $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$

Cuprite: $Cu_2O + H_2SO_4 \rightarrow CuSO_4 + Cu + H_2O$

Carbonates

Azurite: $2CuCO_3{\cdot}Cu(OH)_2 + 3H_2SO_4 \rightarrow 3CuSO_4 + 2CO_2 + 4H_2O$

Malachite: $CuCO_3.Cu(OH)_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + CO_2 + 3H_2O$

Silicates

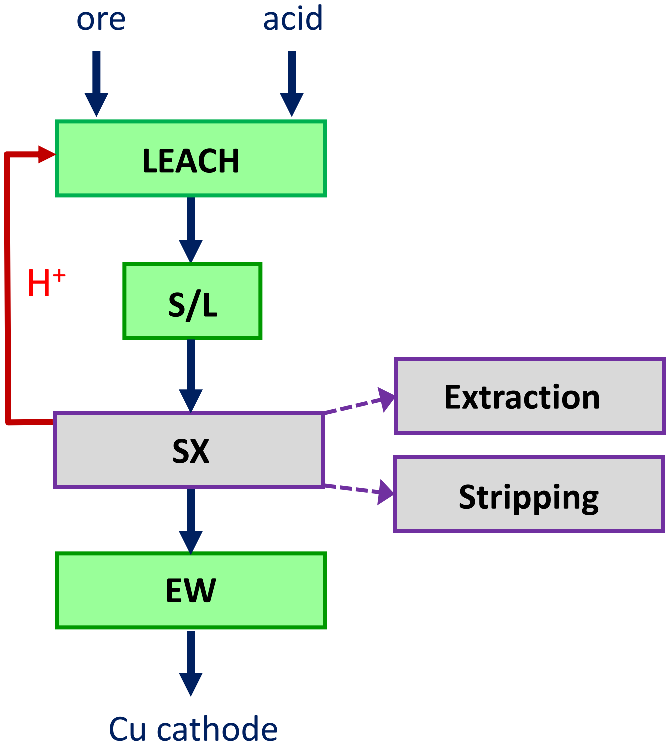
Chrysocolla: $CuO{\cdot}SiO_2 + H_2SO_4 \rightarrow CuSO_4 + SiO_2{\cdot}nH_2O + (3-n)H_2O$

Secondary sulfides

Chalcocite: $Cu_2S + ½\, O_2 + H_2SO_4 \rightarrow CuSO_4 + CuS + H_2O$

Covellite: $CuS + ½\, O_2 + H_2SO_4 \rightarrow CuSO_4 + S + H_2O$

Copper L-SX-EW



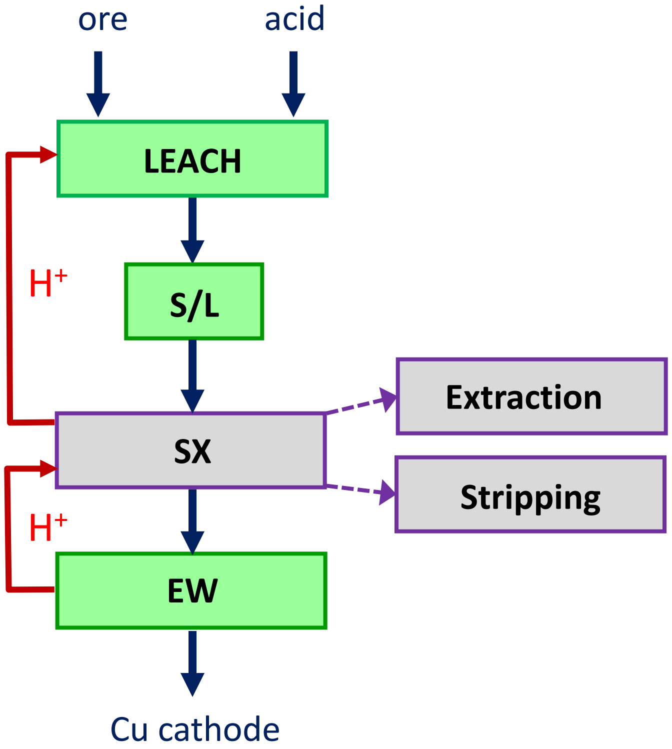
Leach

$CuO + 2H^+ \rightarrow Cu^{2+} + H_2O$

Solvent extraction

Extraction: $Cu^{2+} + 2RH \rightarrow CuR_2 + 2H^+$

Copper L-SX-EW



Leach

$CuO + 2H^+ \rightarrow Cu^{2+} + H_2O$

Solvent extraction

Extraction: $Cu^{2+} + 2RH \rightarrow CuR_2 + 2H^+$

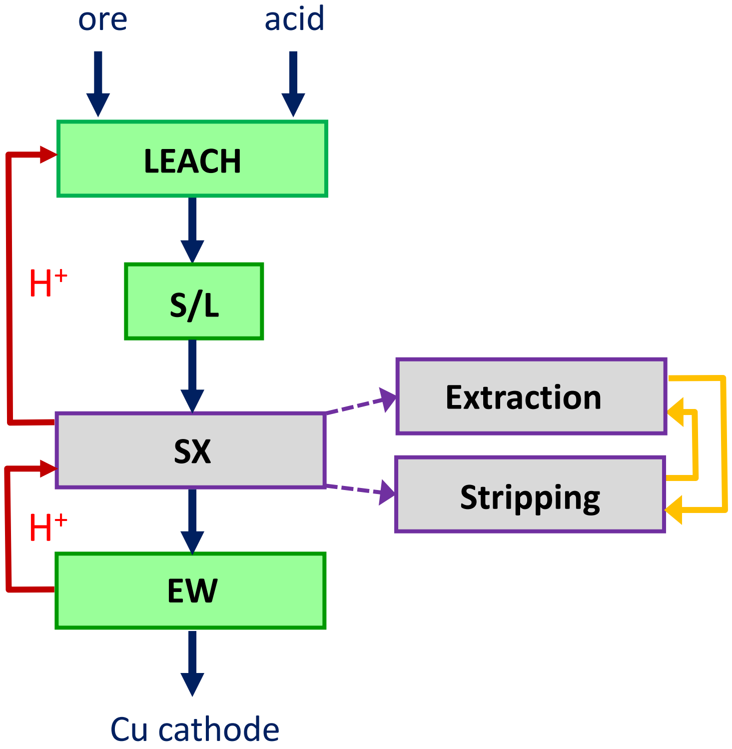
Stripping: $CuR_2 + 2H^+ \rightarrow Cu^{2+} + 2RH$

Electrowinning

Cathode: $Cu^{2+} + 2e \rightarrow Cu$

Anode: $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e$

Copper L-SX-EW



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Cathode: $Cu^{2+} + 2e \rightarrow Cu$

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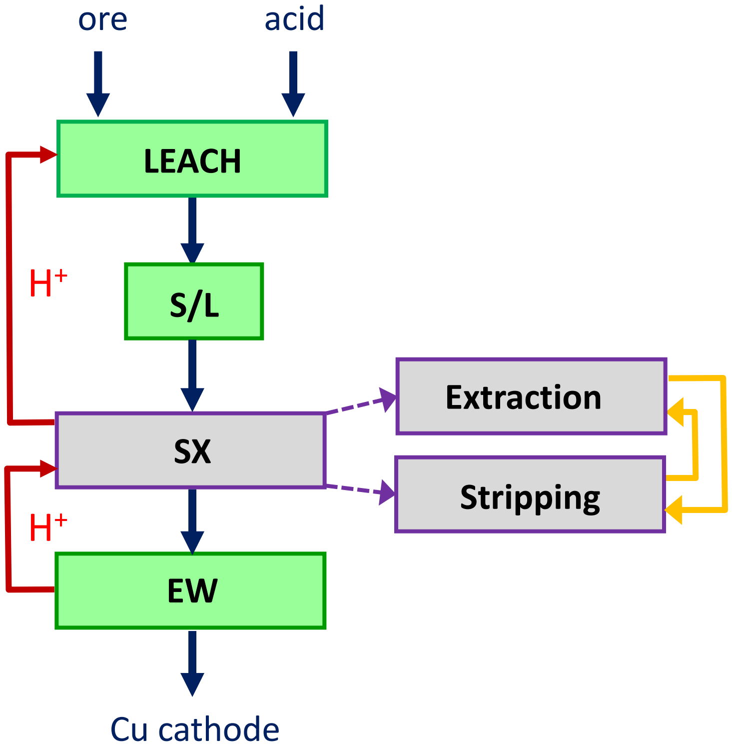
Principle 1: Regenerate reagents



Leach

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Solvent extraction

Extraction: $Cu^{2+} + 2RH \rightarrow CuR_2 + 2H^+$

Stripping: $CuR_2 + 2H^+ \rightarrow Cu^{2+} + 2RH$

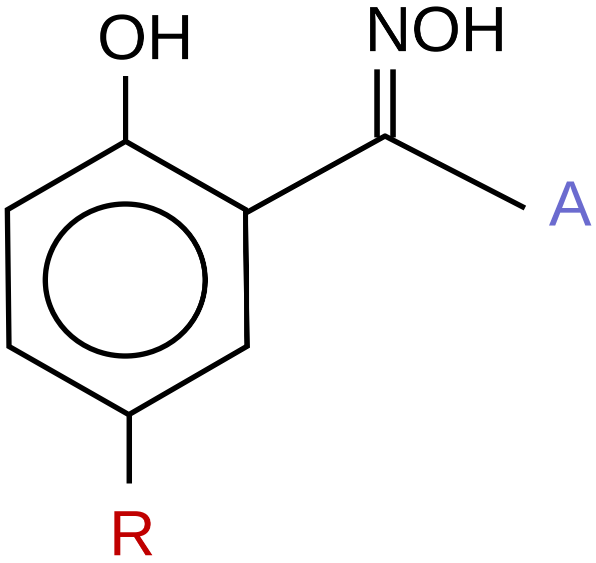
Electrowinning

Cathode: $Cu^{2+} + 2e \rightarrow Cu$

Anode: $H_2O \rightarrow 2H^+ + ½O_2 + 2e$

Modern extractants

Oxime functionality

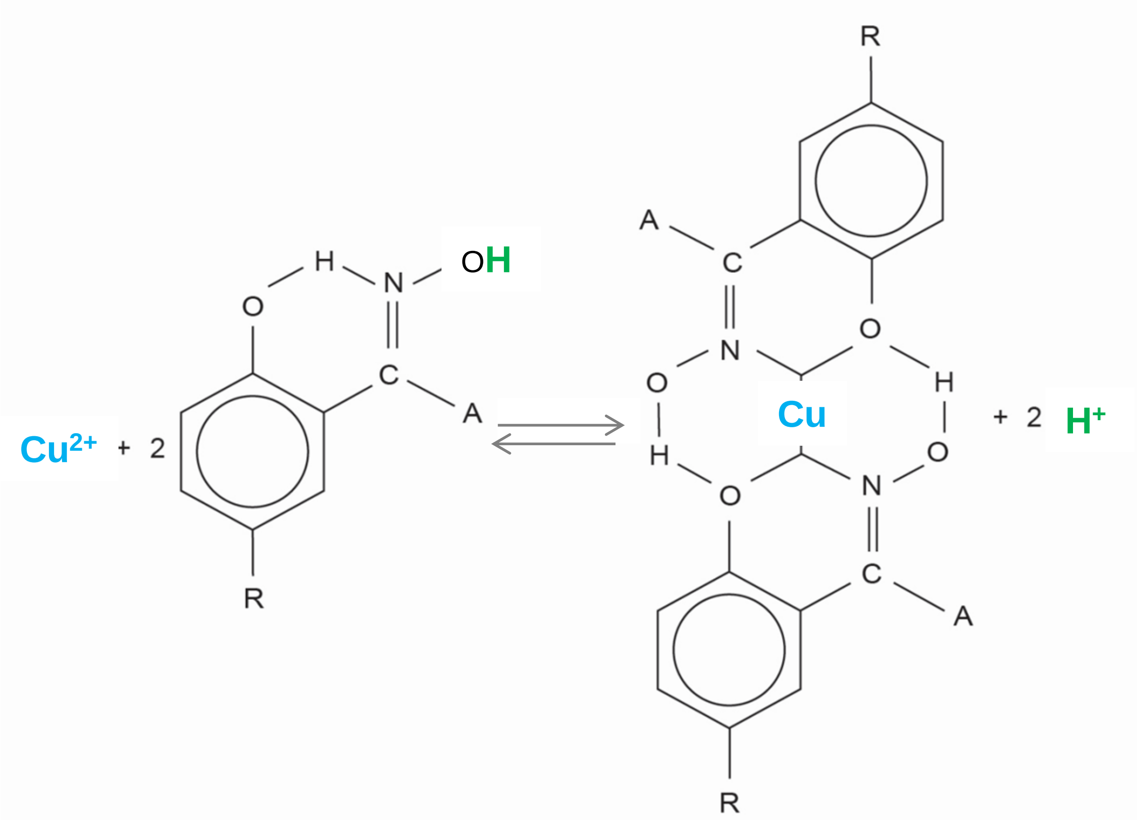


A = H for aldoximes

A = CH_3 for ketoximes

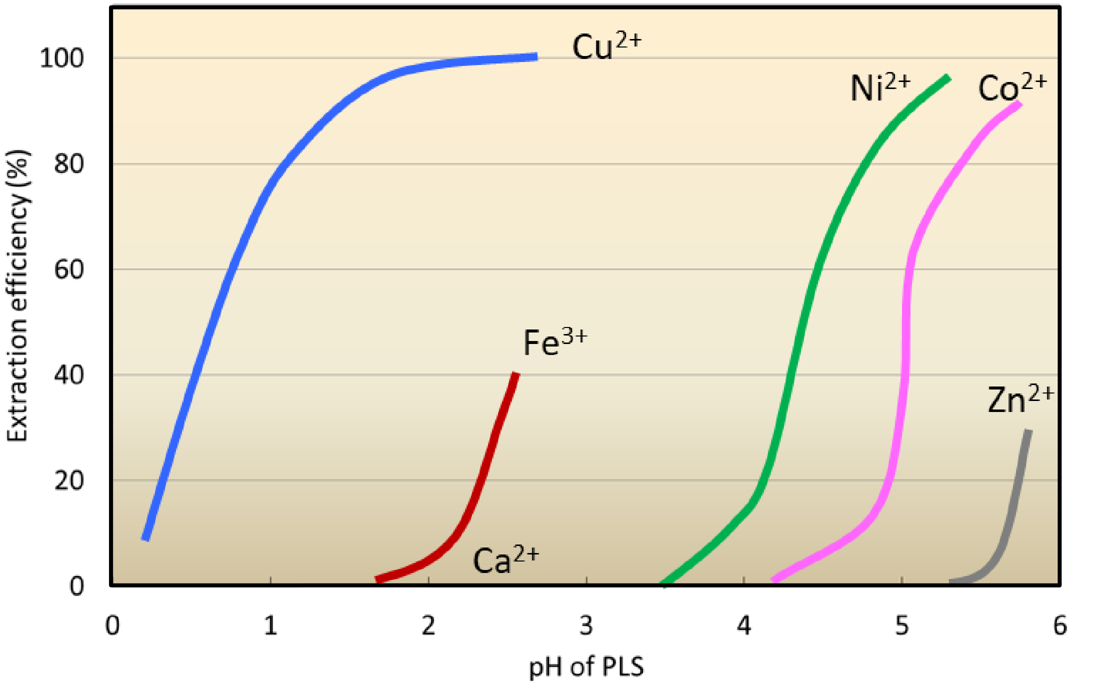
R = C_9H_{19}

Chemistry of copper extraction



Chelation: Greek – pincers

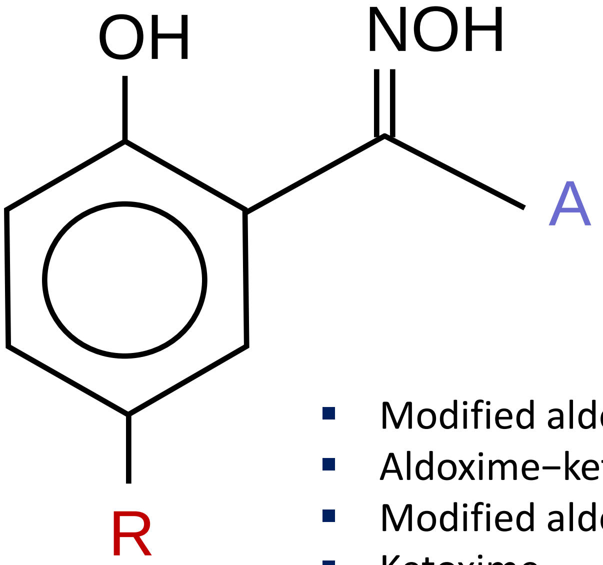
Chemical selectivity of oximes



- High selectivity over base metal cations
- Strong extraction even at low pH
- No interstage neutralisation required
- No Na deportment to raffinate

Data: BASF

Principle 10: Minimise chemical diversity



- Modified aldoximes
- Aldoxime–ketoxime
- Modified aldoxime–ketoxime
- Ketoxime
- C9 chemistry

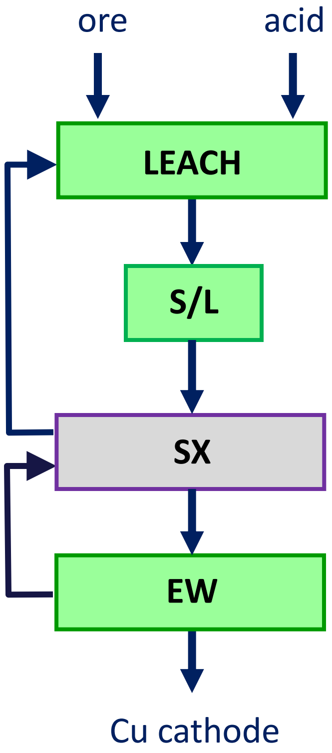
BASF We create chemistry

SYENSQO

KOPPERCHEM 康普化學

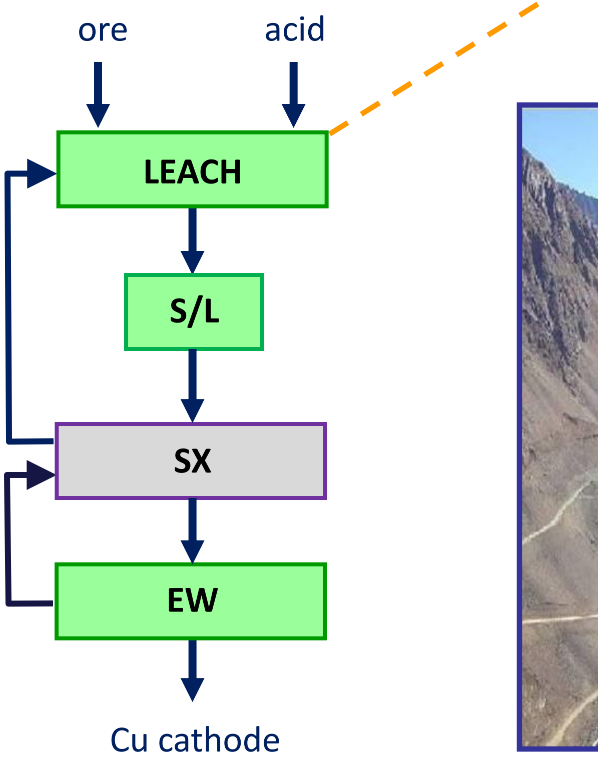
COPPER CHEMICALS

SX enabling the versatility of L-SX-EW



EW requires 45–50 g/L Cu

Versatility of L-SX-EW



Dump leach

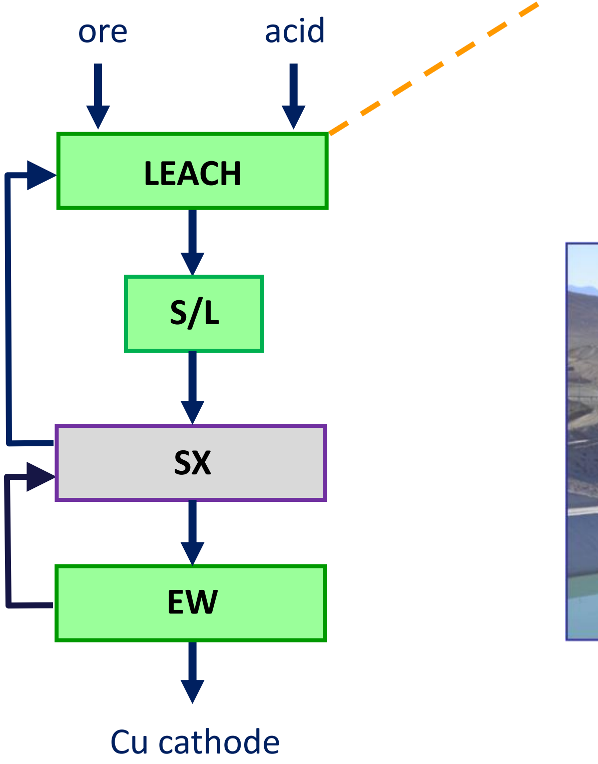
Cu in PLS (g/L)
0.5 – 3

- Low-grade ROM ore (< 0.5% Cu)
- Rock size up to ~ 500 mm

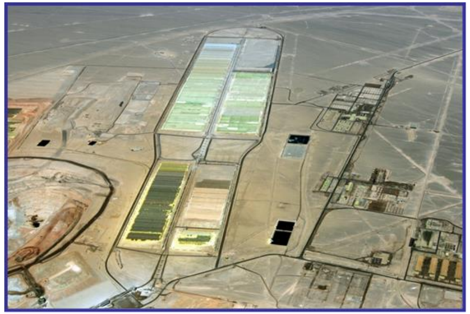
Los Bronces, Chile

Photograph: Anglo American

Versatility of L-SX-EW

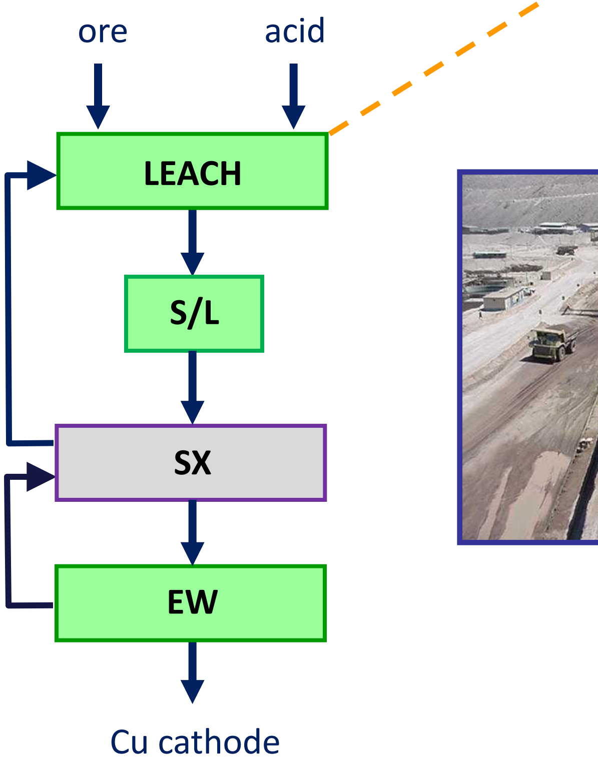


	Cu in PLS (g/L)
Dump leach	0.5 – 3
Heap leach	1.5 – 8



Atacama Desert, Chile

Versatility of L-SX-EW



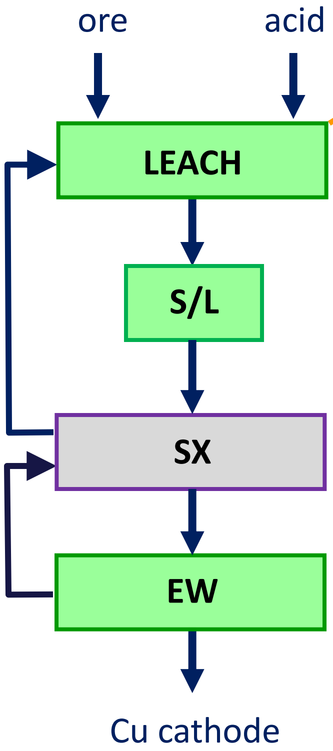
	Cu in PLS (g/L)
Dump leach	0.5 – 3
Heap leach	1.5 – 8
Vat leach	6 – 40

Mantos Blancos, Chile

Mina Justa, Peru

Photographs: Anglo American, Ausenco

Versatility of L-SX-EW

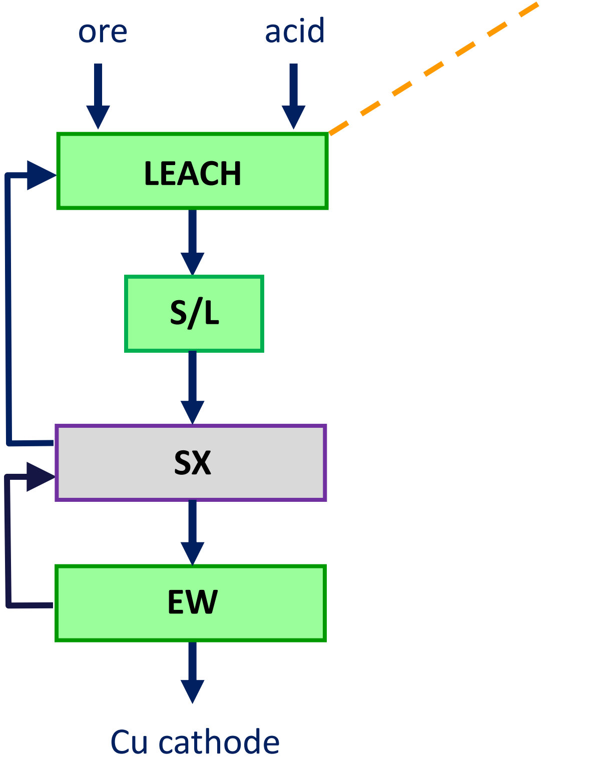


	Cu in PLS (g/L)
Dump leach	0.5 – 3
Heap leach	1.5 – 8
Vat leach	6 – 40
In situ leach	0.5 – 2

Florence, AZ

Photographs: Arizona Geological Survey, Mining.com

Versatility of L-SX-EW

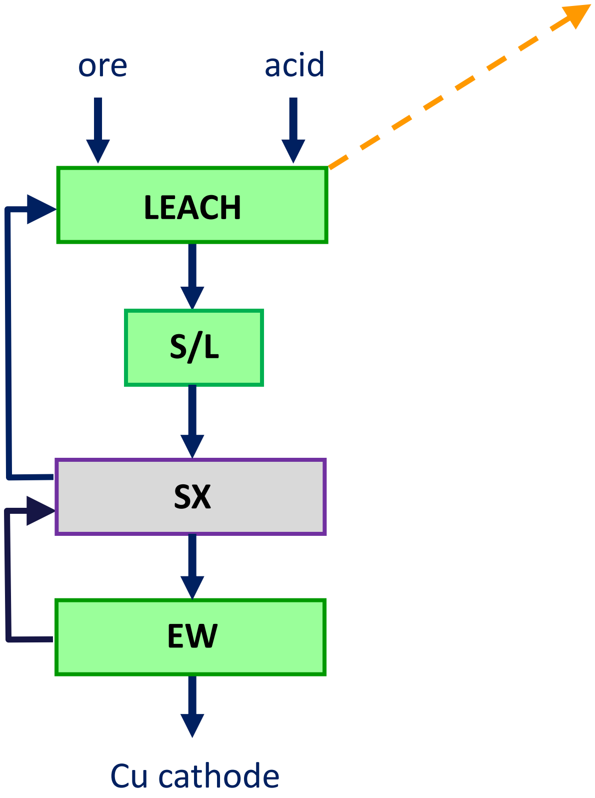


	Cu in PLS (g/L)
Dump leach	0.5 – 3
Heap leach	1.5 – 8
Vat leach	6 – 40
In situ leach	0.5 – 2
Agitation leach	2 – 30

Kansanshi, Zambia

Photograph: First Quantum Minerals

Versatility of L-SX-EW

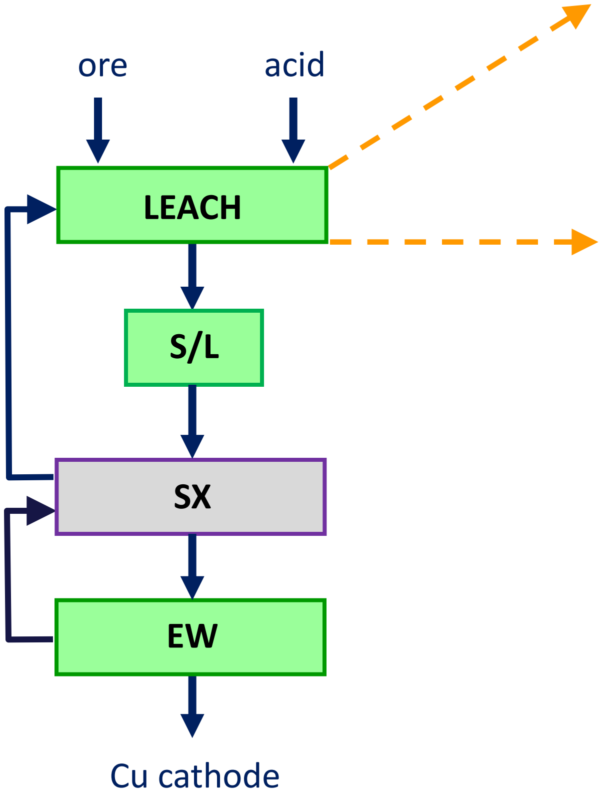


	Cu in PLS (g/L)
Dump leach	0.5 – 3
Heap leach	1.5 – 8
Vat leach	6 – 40
In situ leach	0.5 – 2
Agitation leach	2 – 30
Pressure leach	25 – 80

Kansanshi, Zambia

Photograph: First Quantum Minerals

Versatility of L-SX-EW

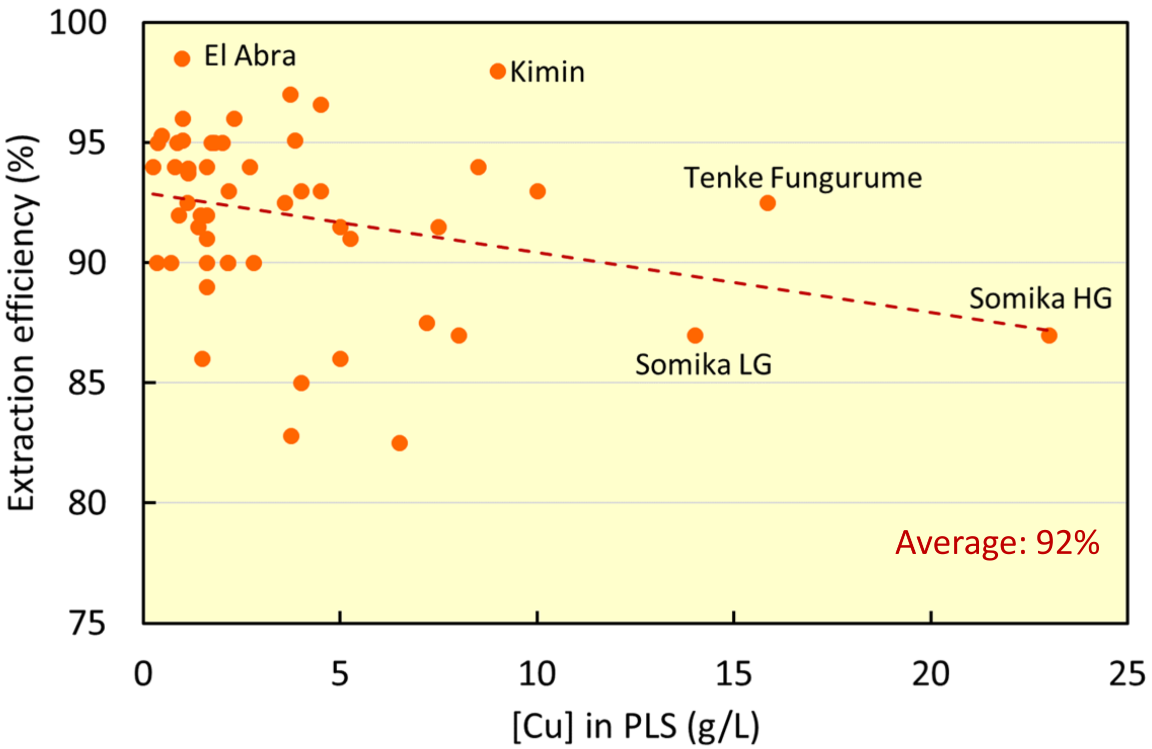


	Cu in PLS (g/L)
Dump leach	0.5 – 3
Heap leach	1.5 – 8
Vat leach	6 – 40
In situ leach	0.5 – 2
Agitation leach	2 – 30
Pressure leach	25 – 80
SX output:	45 – 50
	EW

LME Grade A cathode > 99.99% purity

Photograph: Kansanshi

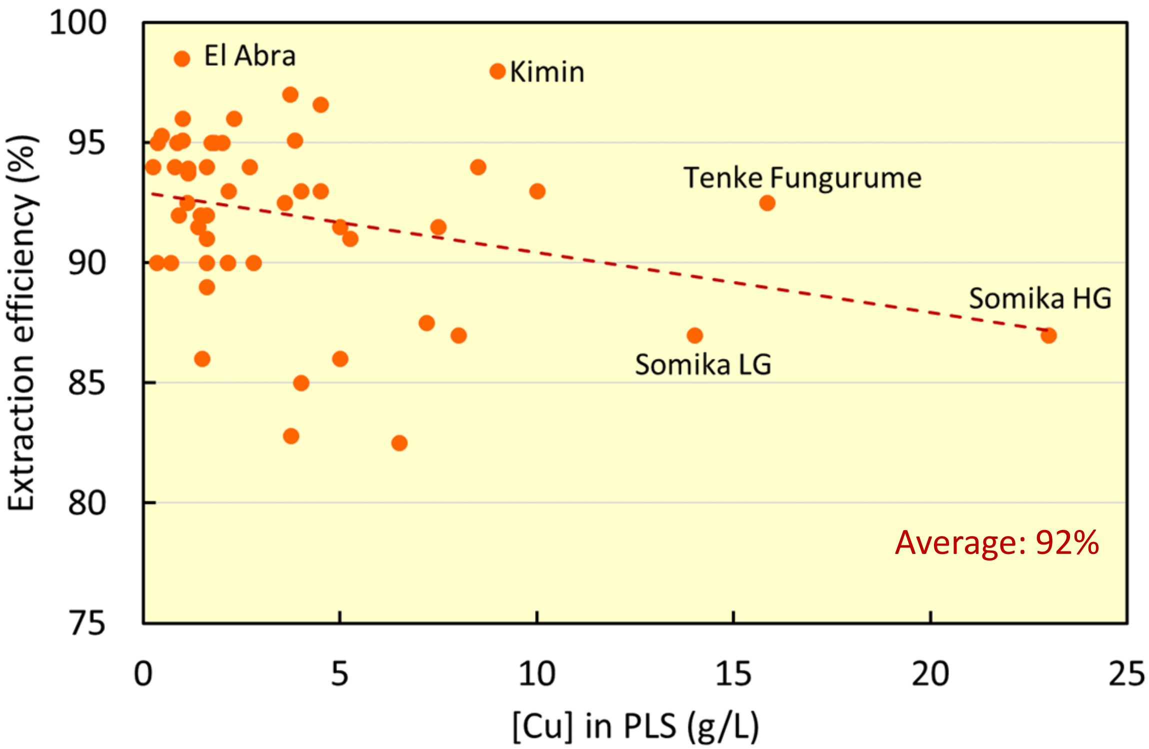
Extraction efficiency



High extraction efficiency for PLS [Cu] ranging two orders of magnitude

Cu SX global survey, Sole et al. (2022)

Principle 10: Minimise chemical diversity



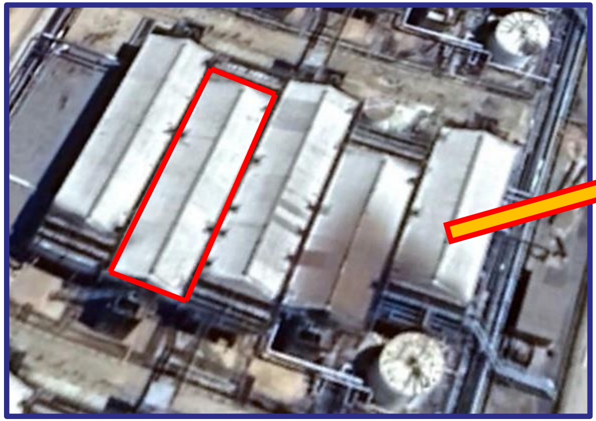
High extraction efficiency for PLS [Cu] ranging two orders of magnitude

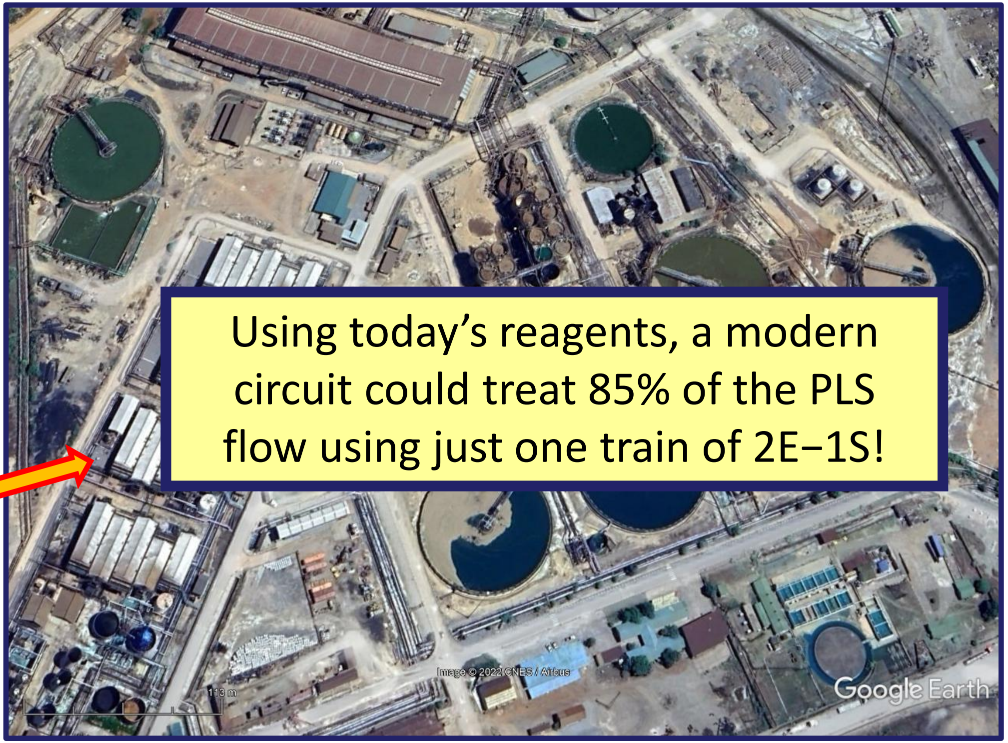
Cu SX global survey, Sole et al. (2022)

Modern oxime extractant formulations

Nchanga Tailings Leach Plant,
Konkola Copper Mines, Zambia
(1974)

4 × 3E−2S SX trains



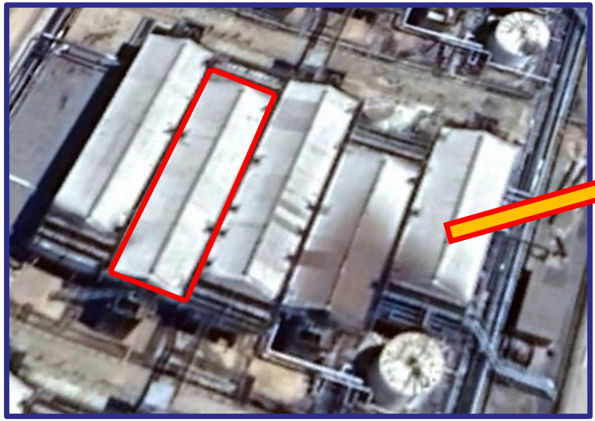


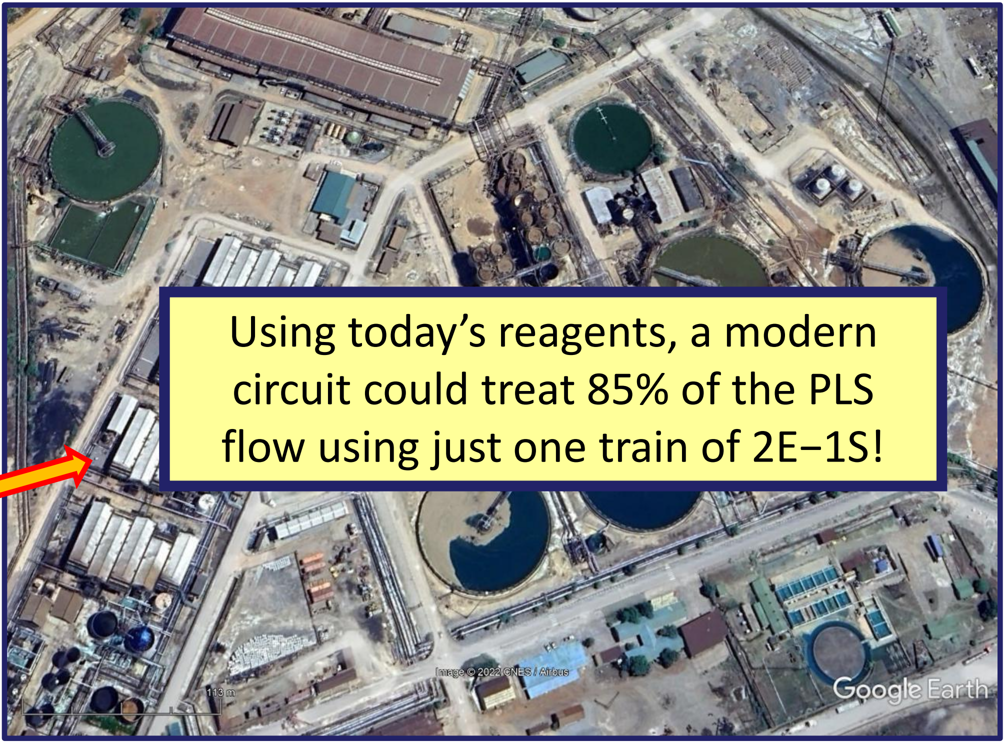
Photograph: GoogleEarth

Principle 4: Maximise space efficiency

Nchanga Tailings Leach Plant,
Konkola Copper Mines, Zambia
(1974)

4 × 3E-2S SX trains

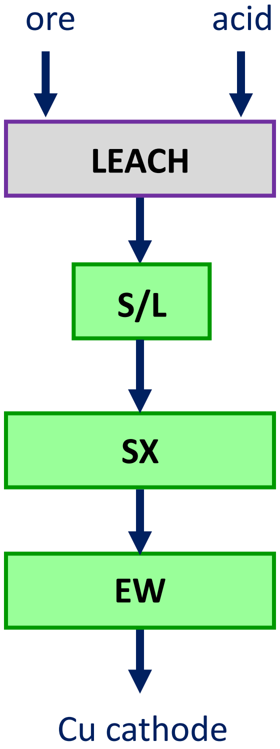




Using today's reagents, a modern circuit could treat 85% of the PLS flow using just one train of 2E−1S!

Photograph: GoogleEarth

Impurities in leach solution



Carbonates

Calcite: $CaCO_3 + H_2SO_4 \rightarrow \mathbf{CaSO_4} + CO_2 + H_2O$

Dolomite: $CaMg(CO_3)_2 + 2H_2SO_4 \rightarrow \mathbf{CaSO_4} + MgSO_4 + 2CO_2 + 2H_2O$

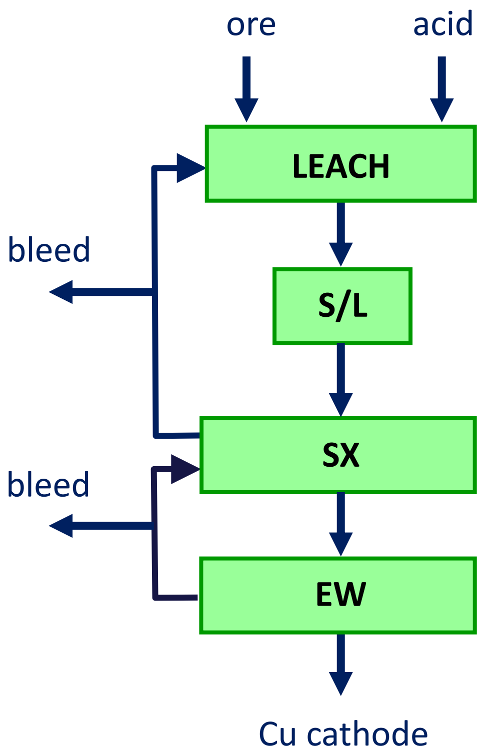
Silicates

Chrysocolla: $CuO{\cdot}SiO_2 + H_2SO_4 \rightarrow CuSO_4 + \mathbf{SiO_2{\cdot}\mathit{n}H_2O} + (3-n)H_2O$

Other acid-soluble impurities

Fe, Al, Mn,...

Process bleed streams

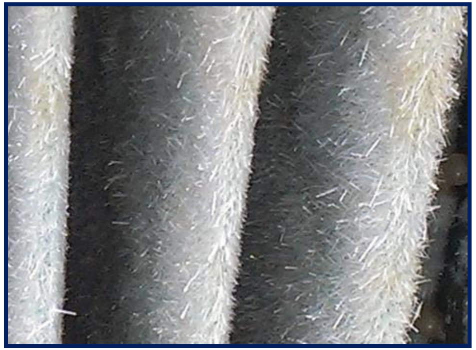


- Bleed for byproduct recovery
  - Co
- Bleed for impurity build-up to avoid detrimental downstream effects
  - Cl, Mn, Fe, Ca, Si
- Loss of valuable components
  - H_2SO_4, Co, Cu, …
- Return to process?

Impurities in process water return

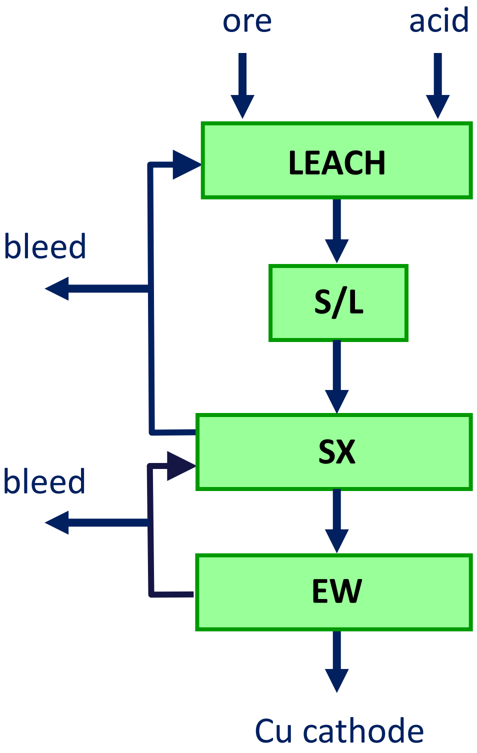
- Ca saturation
- Suspended solids
- Organic contaminants
  - – sewage, oils and grease, humic acids

Gypsum crystals formed on Cu EW anodes owing to Ca saturation of electrolyte



Gypsum accumulation bending steel structure of activated carbon electrolyte filter

Principle 2: Close water loops – *with care*



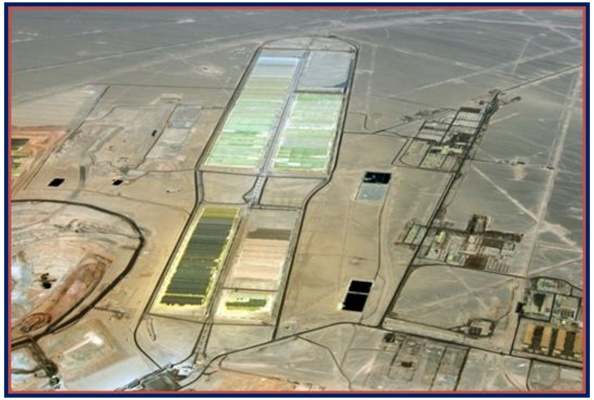
- Bleed for byproduct recovery
  - Co
- Bleed for impurity build-up to avoid detrimental downstream effects
  - Cl, Mn, Fe, Ca, Si
- Loss of valuable components
  - H_2SO_4, Co, Cu, …
- Return to process?

Principle 4: Maximise space efficiency

Heap leaching

Chile, SW USA

Permanent heap
Mantos Blancos, Chile



Dynamic heaps
Spence, Chile

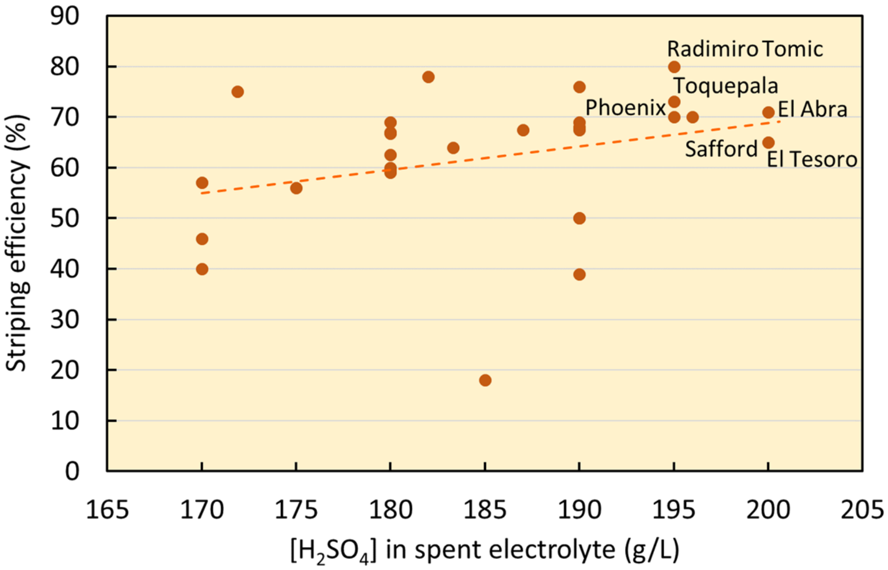
Principle 4: Maximise space efficiency

SX mixer-settlers

- Large settling area
  - up to 25 m × 30 m

Principle 4: Maximise space efficiency

Stripping efficiency of oximes

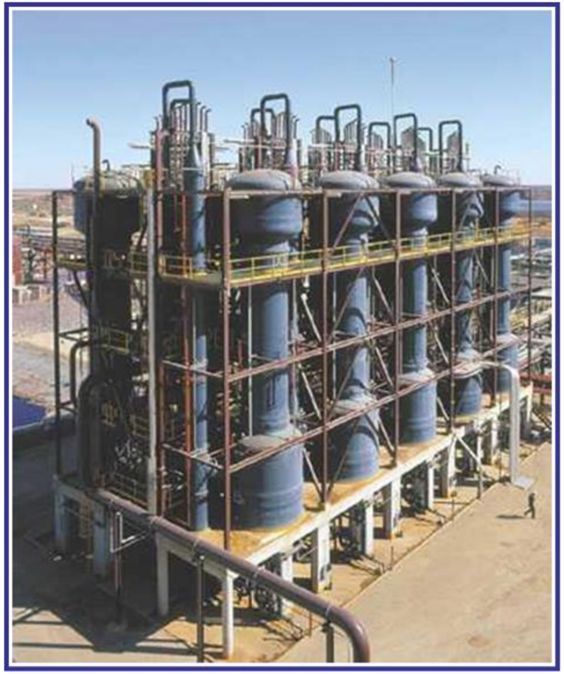


- Typically 50%−70%
- Large dead inventory of Cu on SO

- Higher SE acid concentration
  - Increase hydrolytic degradation
  - Crud formation
  - Organic material to tailings

Global Cu SX survey, Sole et al. (2022)

Principle 4: Maximise space efficiency



Uranium SX circuit, Olympic Dam, Australia

Columns *vs.* mixer-settler?

- Reduce footprint
- Reduce “settler” volume
- Enclosed environment

- Kinetics of Cu SX too slow
- Low number of stages

Photograph: Bateman Litwin

Reagent and design improvements

Parameter*	1970s	2000s
No of extraction stages	4	2
No of stripping stages	2	1
Mixer retention time (min)	3–4	2–3
Cu production (t/a/m^2)	4	16

*Cu SX plants USA and Chile

Kordosky (2002)

Principle 4: Maximise space efficiency

Parameter*	1970s	2000s
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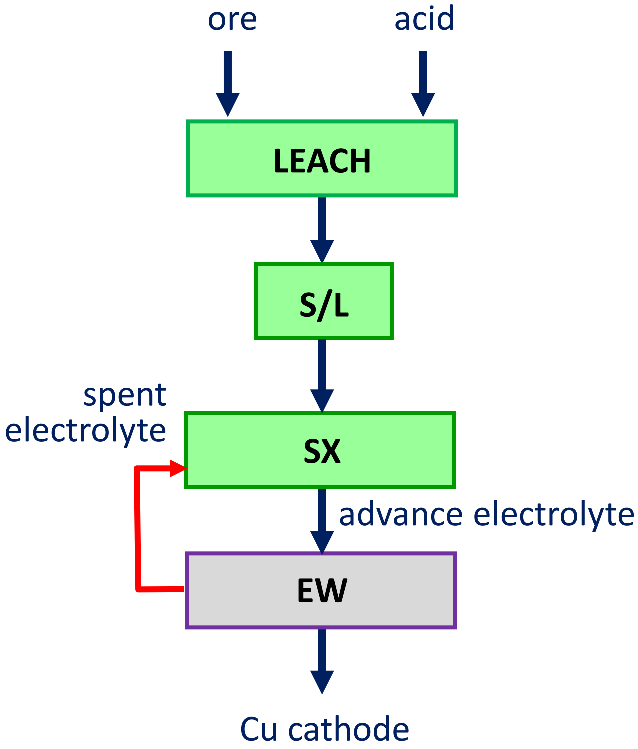
Mixer retention time (min)	3–4	2–3
Cu production ($t/a/m^2$)	4	16

*Cu SX plants USA and Chile

Kordosky (2002)

Principle 8: Electrify where possible



Solvent extraction

Extraction: $Cu^{2+} + 2RH \rightarrow CuR_2 + 2H^+$

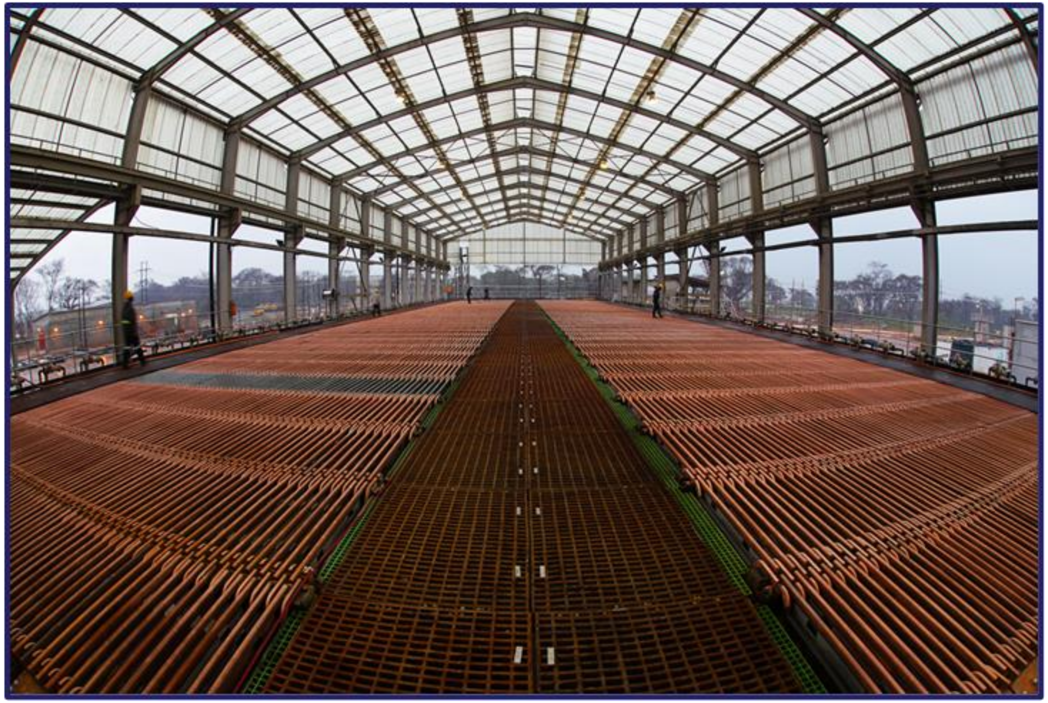
Stripping: $CuR_2 + 2H^+ \rightarrow Cu^{2+} + 2RH$

Electrowinning

Cathode: $Cu^{2+} + 2e \rightarrow Cu$

Anode: $H_2O \rightarrow 2H^+ + ½O_2 + 2e$

Principle 4: Maximise space efficiency



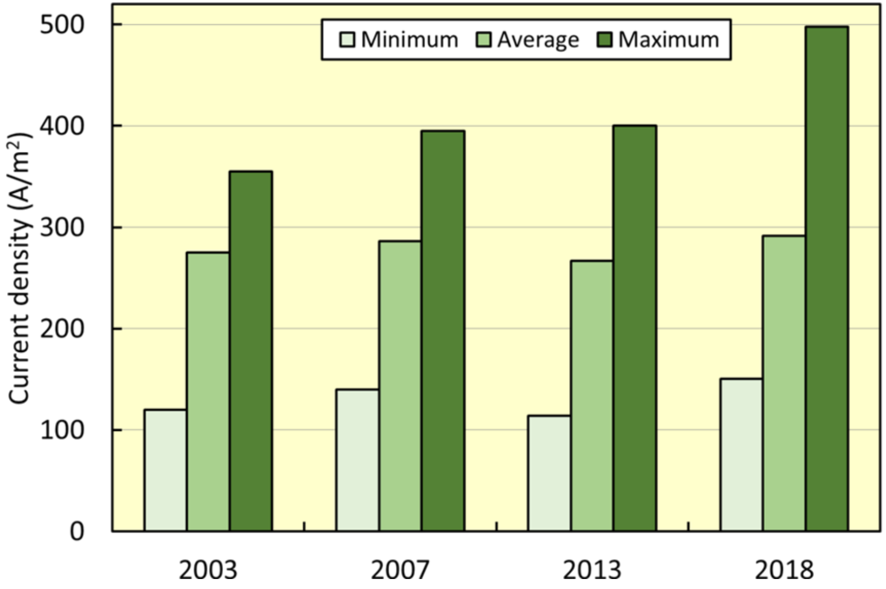
Tankhouse design

- Anode−cathode spacing
- Tankhouse layout
- Electrical layout
- Maximise crane productivity

Photograph: Kansanshi

Principle 4: Maximise space efficiency

Trend to higher current density



Global Cu EW survey, Sole et al. (2019)

Higher current density → higher acid mist production

Acid mist

Anode: $H_2O \rightarrow ½O_2 + 2H^+ + 2e^-$

- Irritation of mucous membranes, causing coughing and difficulty in breathing
- Dental erosion and acute reduction in lung function on long-term exposure
- Throat and lung cancer - classified as Group 1 – carcinogenic to humans

Photograph: Frank Crundwell

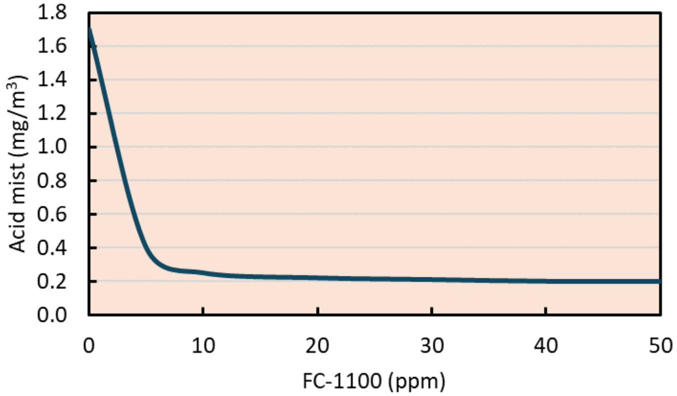
Acid mist suppression/mitigation

- FC-1100 (3M) gave excellent performance at low dosage
  - CFC "forever chemical"

- Natural products (*Saponins*, Mistop, *etc*.) work at low CD
  - Ineffective and degrade above ~250 A/m^2
  - Susceptible to biological growth
    → degradation and poor PST in SX

- Clariant: Floticor 0T, Floticor DC 17382, CAMS 007
  - Used at several African sites

- Protea: EW 1000 and EW 1100
  - Used in Australia, under trial in USA



Data: 3M

Principle 9: Use benign chemicals

- FC-1100 (3M) had excellent performance at low dosage
  - CFC "forever chemical"
- Natural products (*Saponins*, Mistop, *etc*.) work at low CD
  - Ineffective and degrade above ~250 A/m^2
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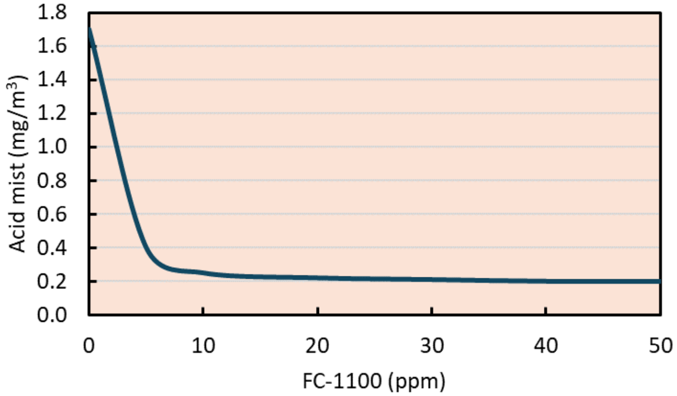
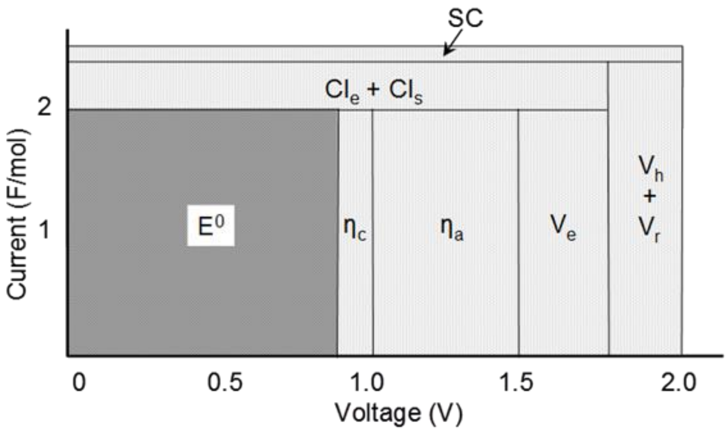


→ No ideal substitute found to date

Data: 3M

Principle 4: Maximise energy efficiency

Contributions to Cu EW power consumption



<u>Voltage components</u>

E^o	:	thermodynamic potential
η	:	overpotentials
V_e	:	Ohmic drop due to electrolyte
V_h	:	Ohmic drop due to hardware
V_r	:	Voltage loss due to rectifier

<u>Current components</u>

nF	:	stoichiometric current (charge)
CI_e	:	current inefficiency due to side reactions
CI_s	:	current inefficiency due to shorts
SC	:	stray currents in tankhouse

Thermodynamic energy requirement (from Faraday's Law): 0.76 kWh/kg

Actual power consumption: ~ 2.0 kWh/kg

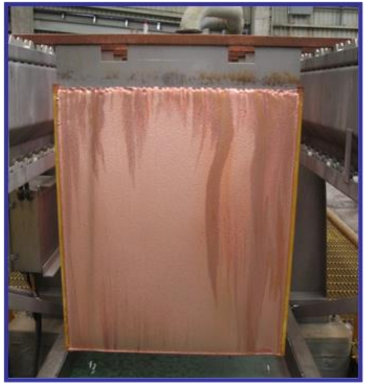
→ Energy efficiency ~ 38%!

From Nicol (2008)

Principle 4: Maximise energy efficiency

- Permanent cathode technology
- Electrical contact design
- Spacers for electrode alignment
- Automated crane handling
- Electronic hot-spot and short detection
- …

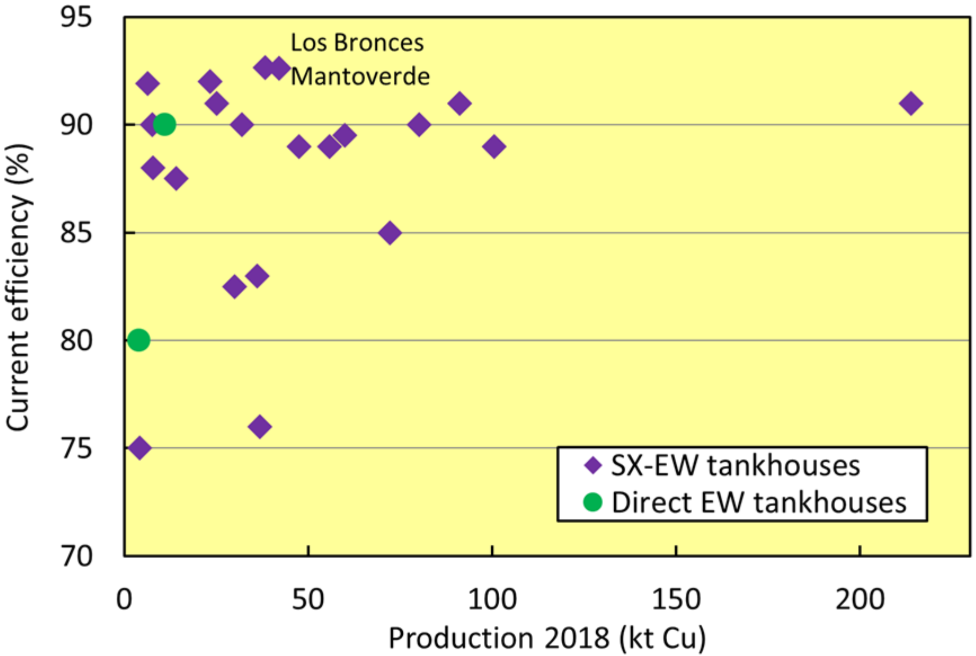




Principle 4: Maximise energy efficiency

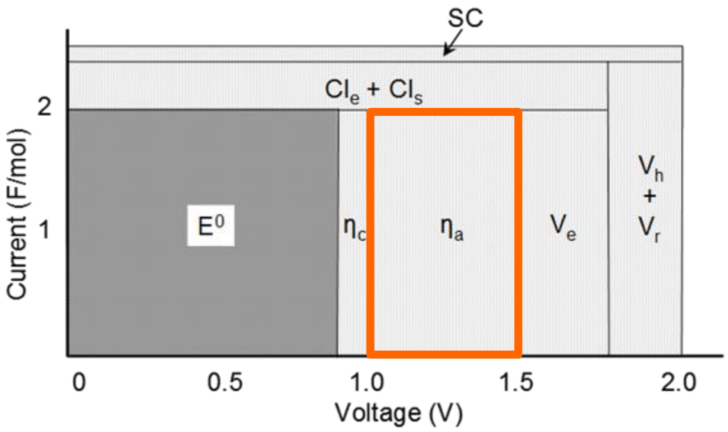
Trends in current efficiency



Global Cu EW survey, Sole et al. (2019, 2022)

Principle 4: Maximise energy efficiency

Contributions to Cu EW power consumption



Voltage components

E^o : thermodynamic potential
η_c : cathode overpotential
η_a : anode overpotential
V_e : Ohmic drop due to electrolyte
V_h : Ohmic drop due to hardware
V_r : Voltage loss due to rectifier

Current components

nF : stoichiometric current (charge)
CI_e : current inefficiency due to side reactions
CI_s : current inefficiency due to shorts
SC : stray currents in tankhouse

From Nicol (2008)

Principle 4: Maximise energy efficiency
Principle 7: Decrease activation energy

Alternative anode material

- Ti mesh coated with precious metal oxide
- Lower η_a for O_2 evolution

- 15% reduction in cell voltage
- 2% increase in CE
- No cell cleaning
- Eliminate health risks of Pb

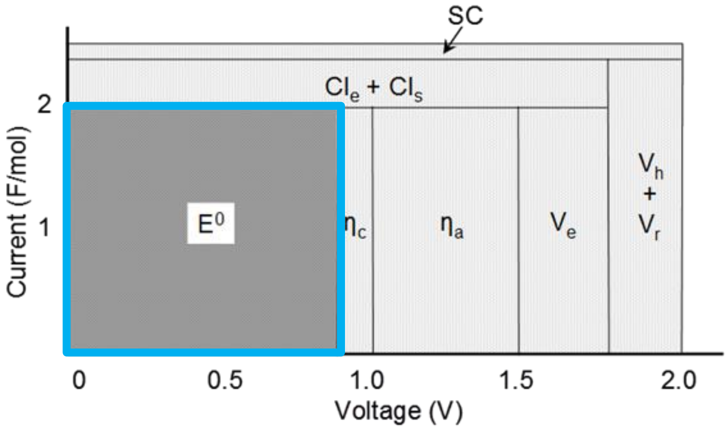
- Commercialised in US, Chile, Norway
- Fragile – prone to shorts
- Expensive – PM recovery

DSA – dimensional stable anode
CTA – coated titanium anode

Photograph: Tim Robinson

Principle 4: Maximise energy efficiency

Contributions to Cu EW power consumption



Voltage components

E^o	**:**	**thermodynamic potential**
η	:	overpotentials
V_e	:	Ohmic drop due to electrolyte
V_h	:	Ohmic drop due to hardware
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Current components

nF	:	stoichiometric current (charge)
CI_e	:	current inefficiency due to side reactions
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SC	:	stray currents in tankhouse

From Nicol (2008)

Principle 4: Maximise energy efficiency

Alternative anode reaction for Cu EW

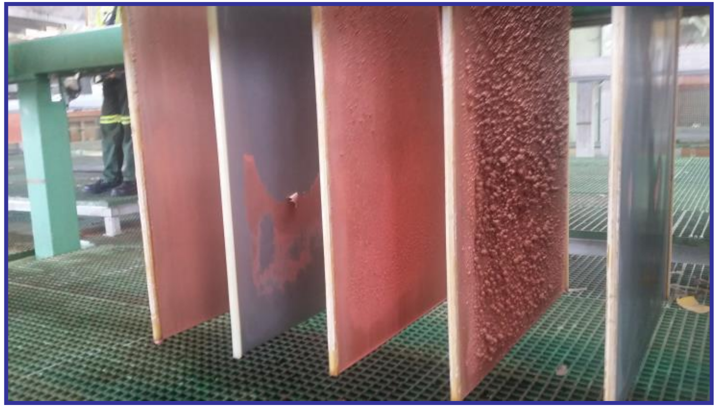
Conventional:	$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e$	$E^0 = -1.23$ V
Alternative:	$Fe^{2+} \rightarrow Fe^{3+} + e$	$E^0 = -0.77$ V
Regeneration:	$2H_2O + SO_2 + 2Fe^{3+} \rightarrow 2Fe^{2+} + H_2SO_4 + 2H^+$	

May et al. (2005); Sandoval et al. (2010)

Principle 3: Prevent waste

Cathode scrap

- Control of EW parameters
- Electrolyte impurities
- General housekeeping in tankhouse



Photographs: Zindaba Zulu, Yolande Stegmann

Principle 3: Prevent waste
Principle 6: Safely dispose of toxic materials

Lead sludge

- Control of EW parameters
- Anode care and maintenance
- General housekeeping in tankhouse
- Recycling of old anodes
- Use of non-lead anode

Photographs: XStrata, RSR Technologies

Principle 9: Use benign chemicals
Principle 6: Safely dispose of toxic materials

Acid mist suppressant – FC-1000

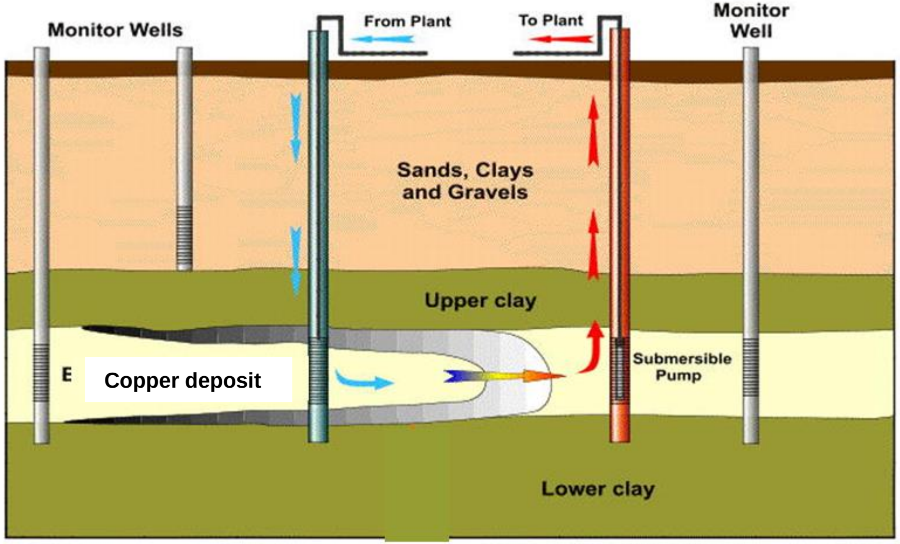
- Fluorocarbon chemicals no longer permitted

Biodegradability of SX diluents

- Traditional use of petrochemical byproducts – inexpensive, low-value distillate
- Synthetic aliphatic diluents – lower toxicity, low odour, biogradeable

Principle 12: Zero-waste mining
Principle 3: Prevent waste

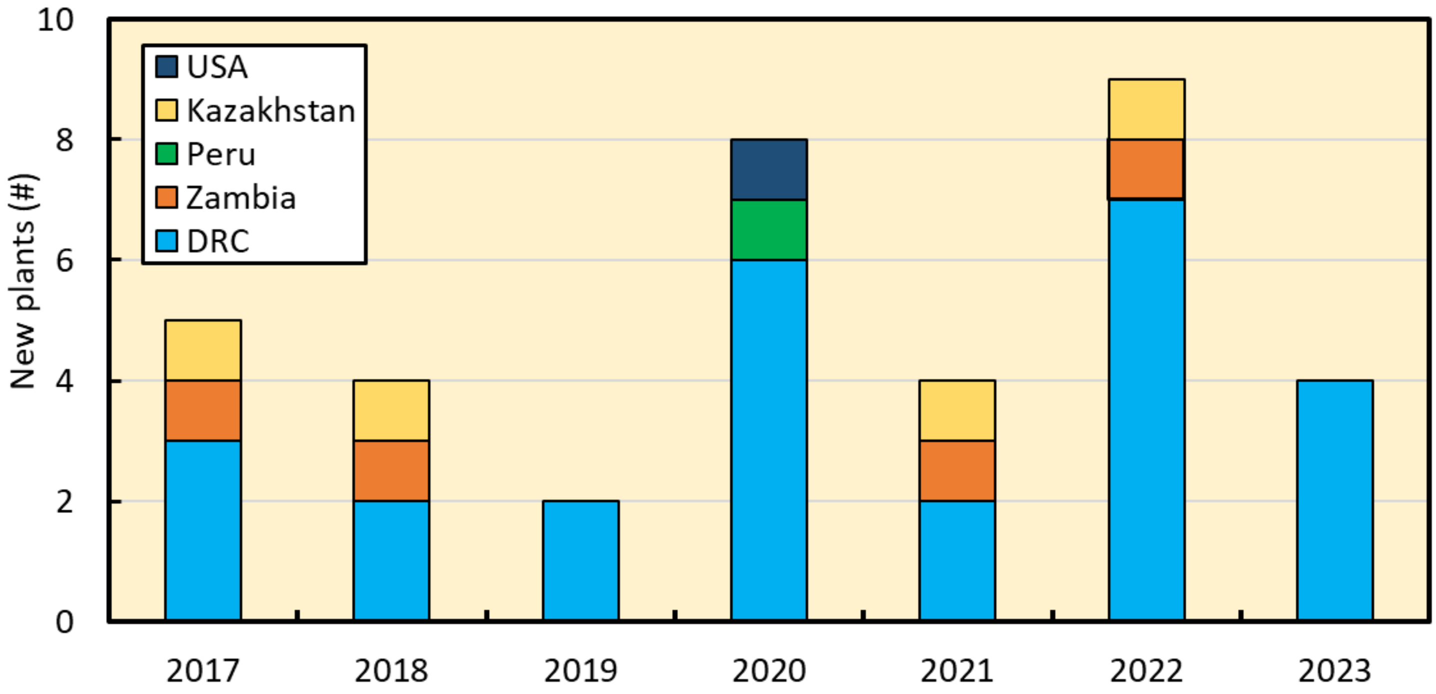
In-situ leaching



Florence, AZ

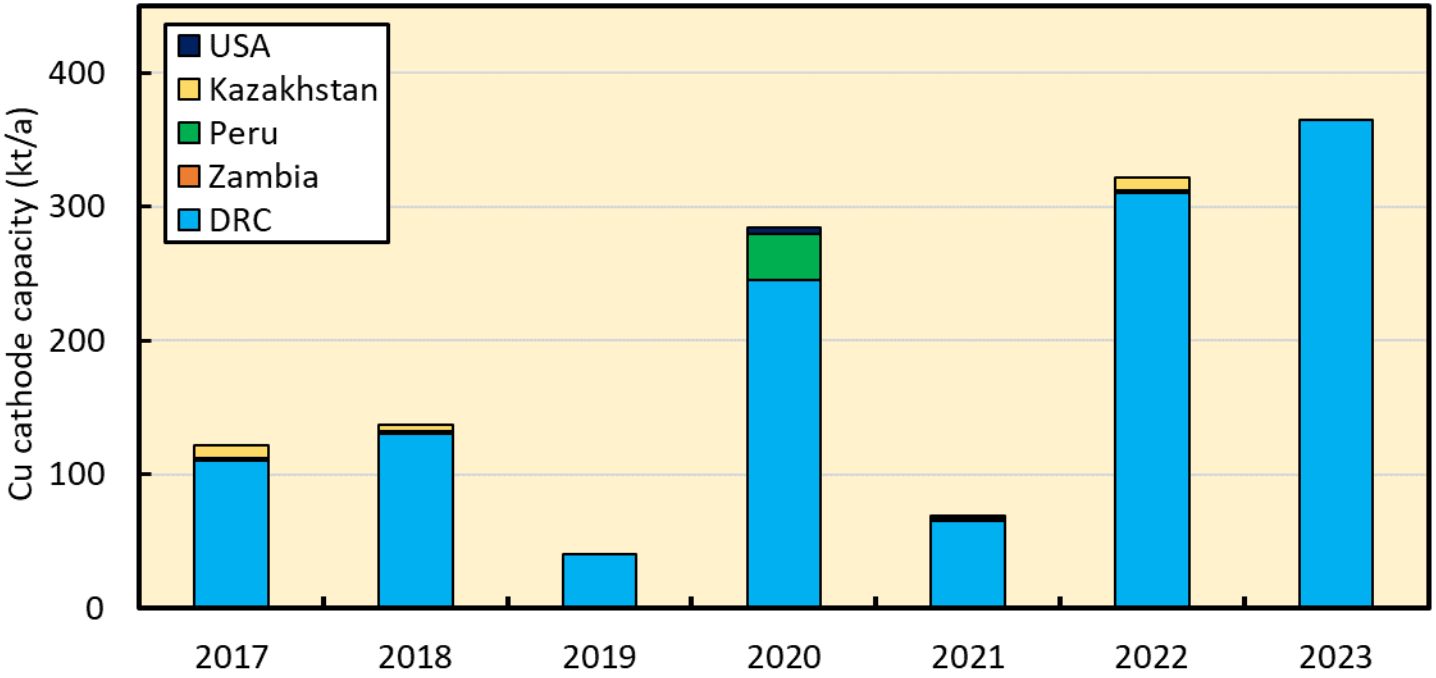
Some further thoughts…

New Cu SX-EW plants worldwide



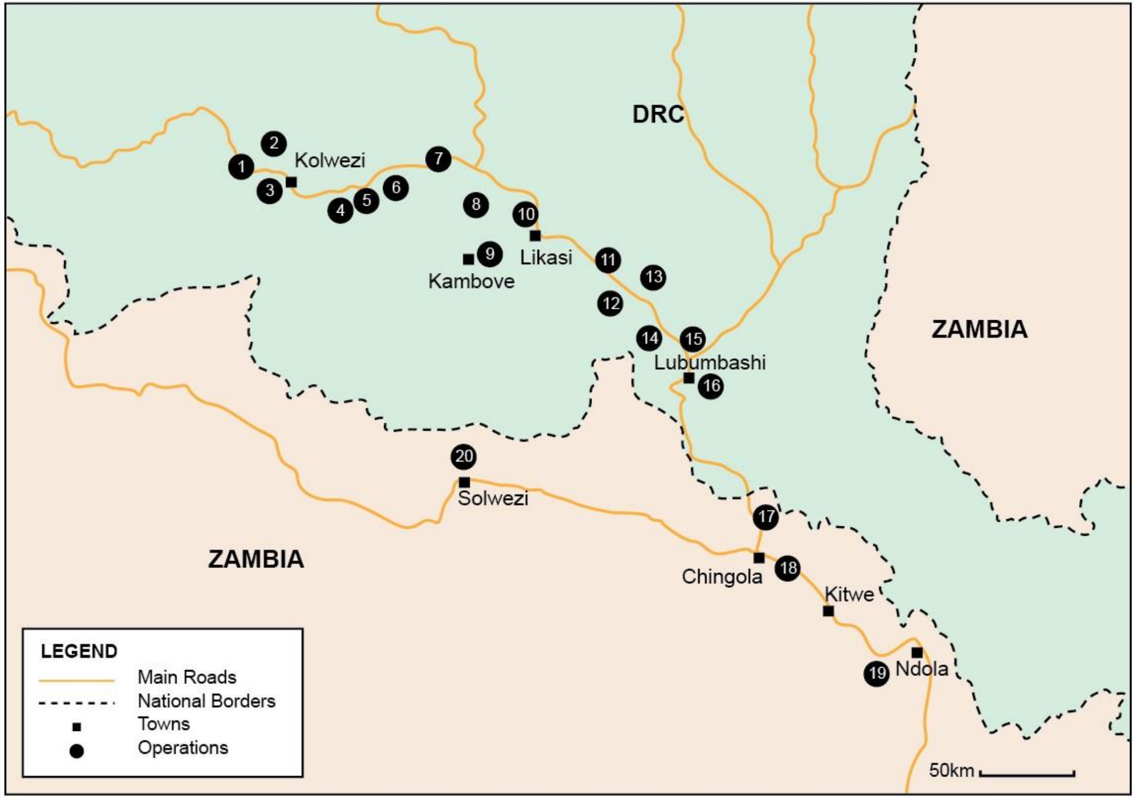
Tinkler & Sole (2023)

New Cu SX-EW capacity



Tinkler & Sole (2023)

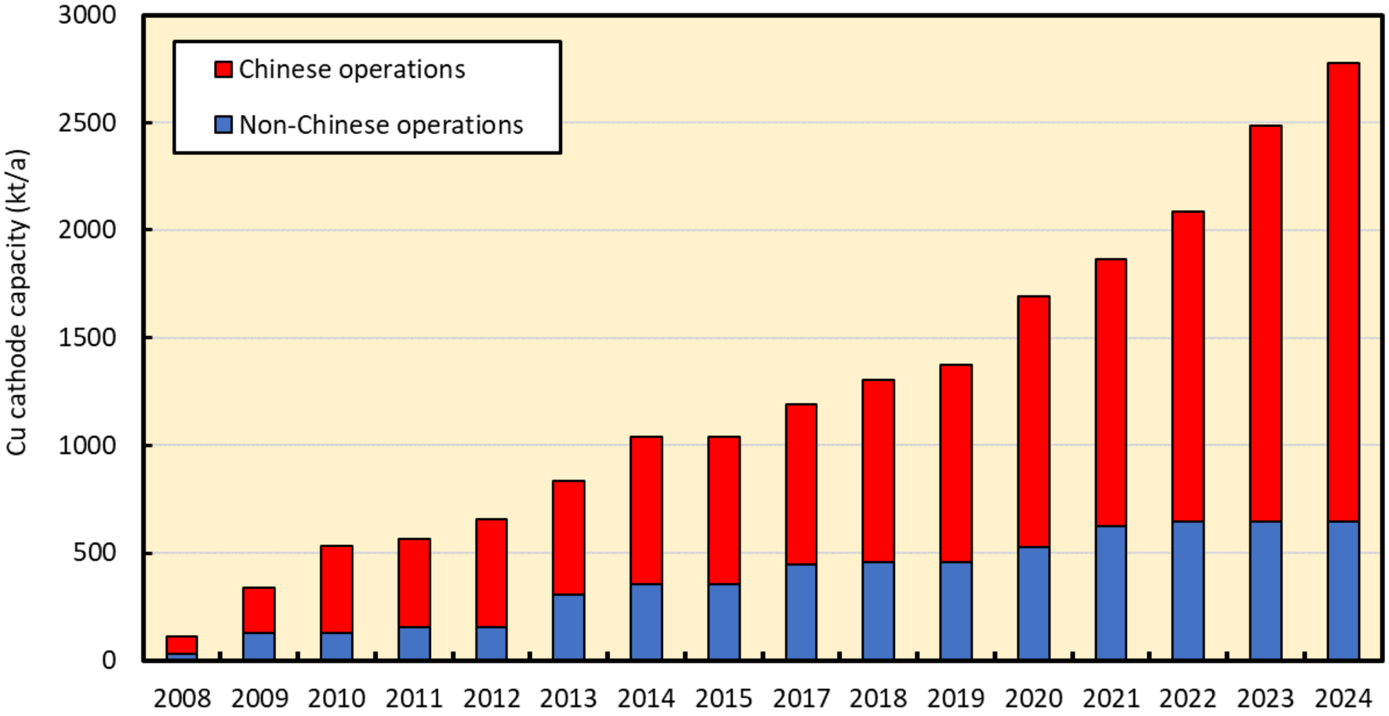
African Copperbelt



- 33% global SXEW Cu (Chile: 34%)
- +50 SXEW operations
- 2.8 Mt/a capacity

Tinkler & Sole (2023)

Copper cathode capacity in DRC



Tinkler & Sole (2023)

ENERGY MINERALS

Xi pledges $51B in funding for Africa

GEOPOLITICS & GEOECONOMICS | SHORT ANALYSIS

Navigating Critical Mineral Supply Chains: the EU's Partnerships with the DRC and Zambia

CSIS | CENTER FOR STRATEGIC & INTERNATIONAL STUDIES

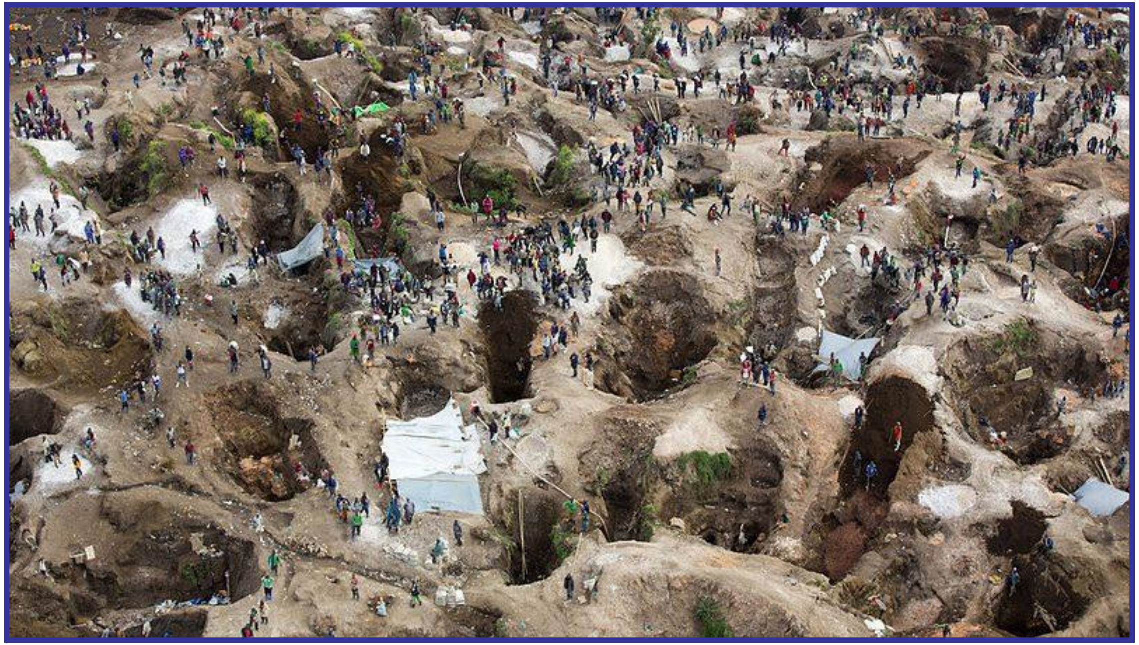
The U.S.-Zambia-DRC Agreement on EV Batteries Production: What Comes Next?

The United States Releases Signed Memorandum of Understanding with the Democratic Republic of Congo and Zambia to Strengthen Electric Vehicle Battery Value Chain

Multinational investment

Restarted ~ 2008

The other side of the fence



- +100 000 artisanal miners
- Estimated 40 000 children
- 65% of the population living on < $ 2.15/d
- 4th poorest country in the world – 2024

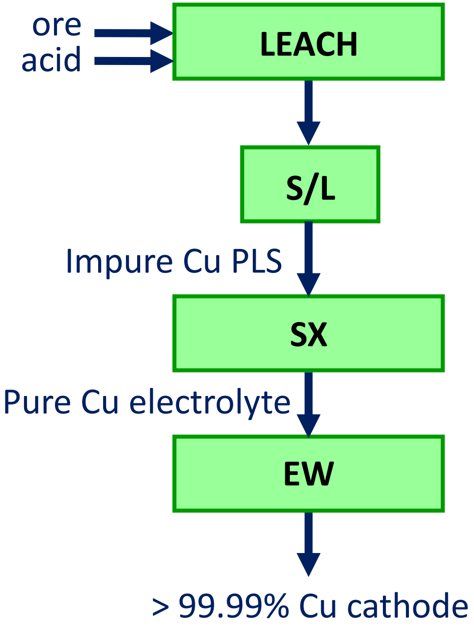
Photograph: Hugh Brown

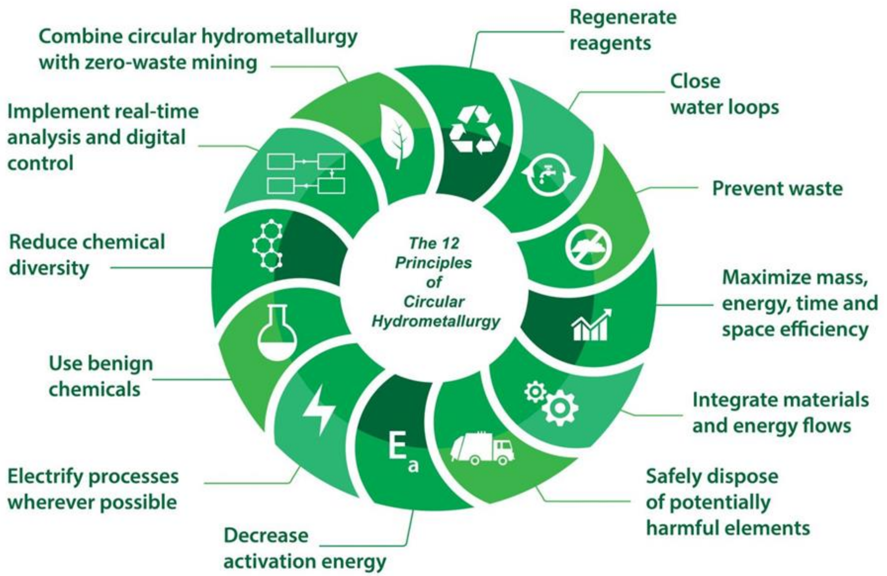
The other side of the fence

Photographs: Hugh Brown


SUSTAINABLE DEVELOPMENT GOALS
1 NO POVERTY
2 ZERO HUNGER
3 GOOD HEALTH AND WELL-BEING
4 QUALITY EDUCATION
5 GENDER EQUALITY
6 CLEAN WATER AND SANITATION
7 AFFORDABLE AND CLEAN ENERGY
8 DECENT WORK AND ECONOMIC GROWTH
9 INDUSTRY, INNOVATION AND INFRASTRUCTURE
10 REDUCED INEQUALITIES
11 SUSTAINABLE CITIES AND COMMUNITIES
12 RESPONSIBLE CONSUMPTION AND PRODUCTION
13 CLIMATE ACTION
14 LIFE BELOW WATER
15 LIFE ON LAND
16 PEACE, JUSTICE AND STRONG INSTITUTIONS
17 PARTNERSHIPS FOR THE GOALS

50 Years of copper L-SX-EW:
A modern circular hydrometallurgy flowsheet





Binnemans & Jones (2023)

Thank you