9^{TH} INTERNATIONAL SECONDARY LEAD & BATTERY RECYCLING CONFERENCE
1 & 2 September 2025
Hilton Kota Kinabalu

Metallurgical Workshop
Evolving Flowsheets in Lead-Acid and Lithium-ion Battery Recycling

dr. Sander Arnout, InsPyro, Belgium

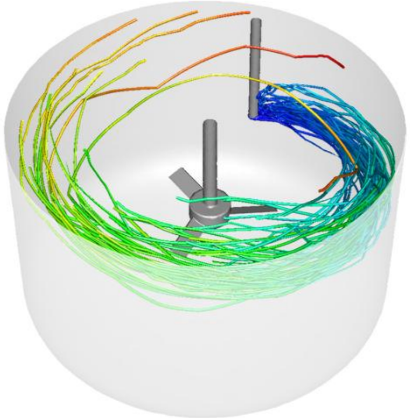
Simulate. Quantify. Optimize.

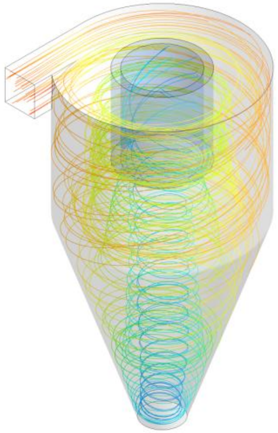
Introduction: InsPyro

B2B consultancy company since 16 years (KU Leuven spin-off 2009 founded and run by PhD's)

Technology neutral, science-based industry support

- Process development & improvement through:
    - Modelling: Thermodynamics, Flowsheet, Fluid Dynamics (CFD)
    - Experiments & Characterization
    - Model and data software integration
    - Industrial experience & network
- Industries:
    - Recycling incl. batteries and residues
    - Non-ferrous metallurgy (pyro and hydro)
    - Steel, cast iron and ferro-alloys
- References: Ecobat, Recylex, Campine, Eramet etc.
- www.inspyro.be

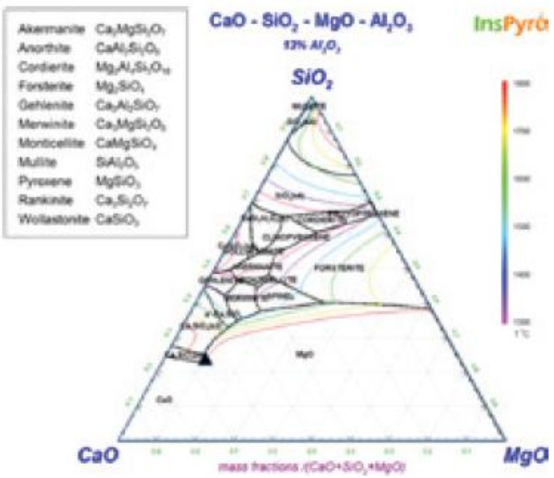




2050 ready metallurgy

Theory

Metallurgical insight, diagrams and thermodynamics software



Simulate

METSIM Flowsheet model

Processes and equipment, plant mass and heat balance

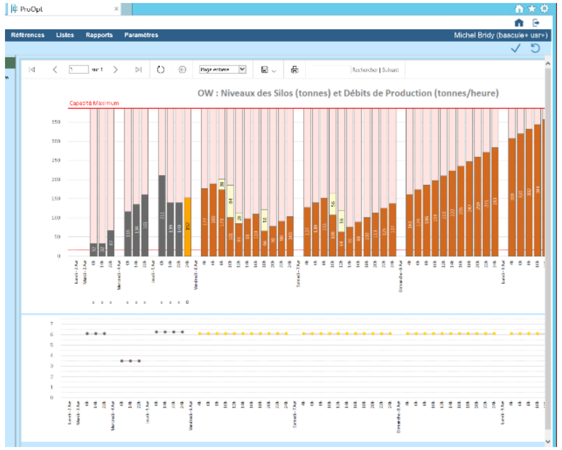
METSIM™

Quantify

ProOpt Advisor

Bring data and models together for fast decisions

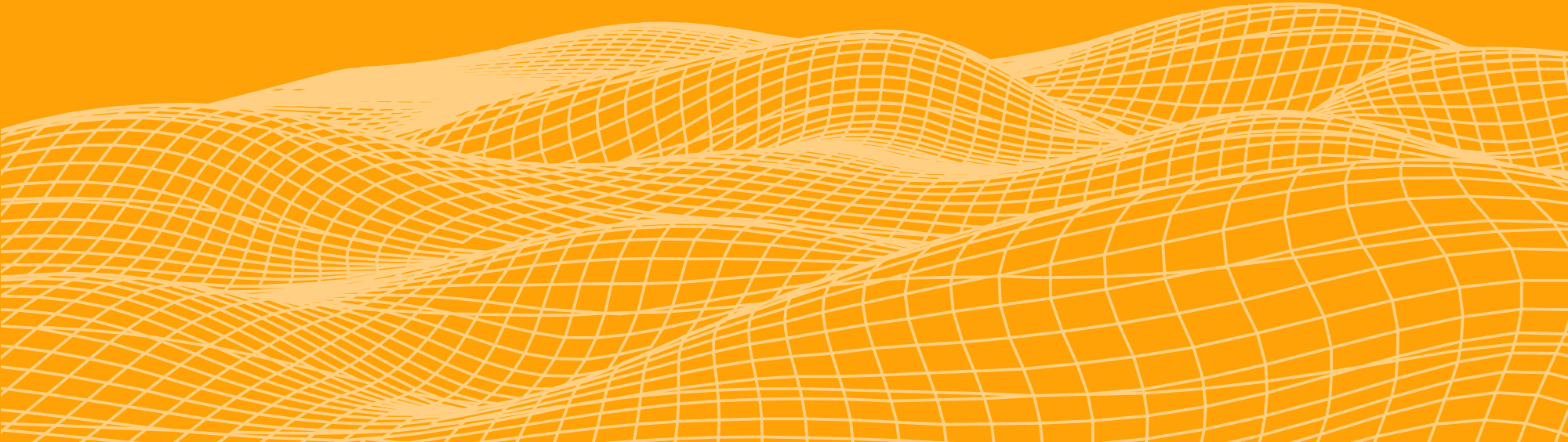
ProOpt International



OW : Niveaux des Silos (tonnes) et Débits de Production (tonnes/heure)

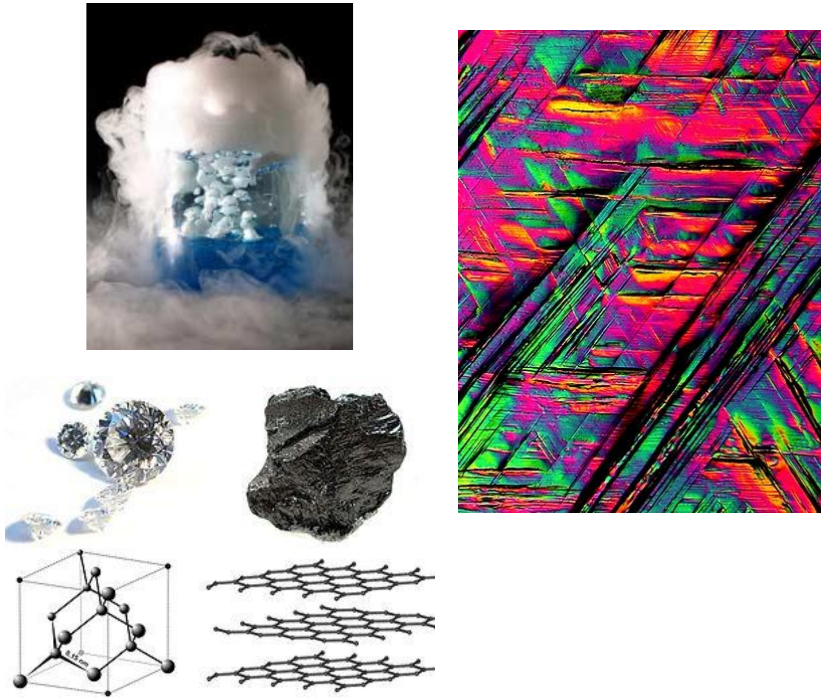
Optimize

Metallurgical basic toolset



Why do we use thermodynamics?

Materials change



Materials react

Thermodynamics tells us what to expect

Gibbs energy mathematical framework

- Thermodynamic equilibrium: theory tells us that systems evolve to the **lowest Gibbs energy** at constant T and P

- By modelling the Gibbs energy of compounds and solutions, we have a **mathematical approach** to compare their stability (which one is preferred in equilibrium)

- We can use **diagrams** such as the Ellingham diagram, to make things visually clear
- We can use **software**, by building on Gibbs energy descriptions (enthalpy+entropy of formation and Cp), e.g. FactSage, ThermoCalc…
- Rather than guessing we make consistent predictions but we can only predict what is known!

Goal: show some examples of useful literature diagrams for battery recycling flowsheets

Order of oxidation and reduction

THE ELLINGHAM DIAGRAM

Ellingham diagram: visualizing reactions

- Gibbs free energy change for the formation of oxides

A metal M reacts with gaseous oxygen at a fixed temperature

$$M_{(s)} + O_{2(g)} \leftrightarrow MO_{2(s)}$$

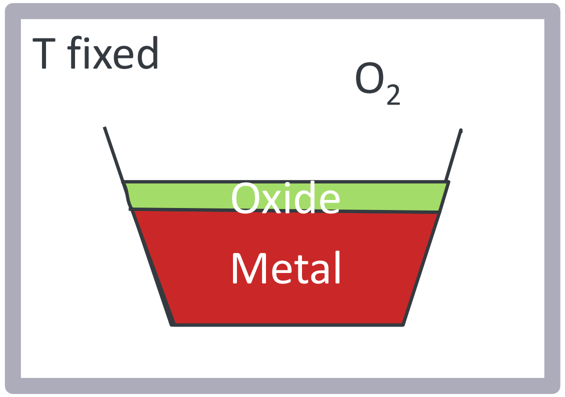
This reactions has a standard Gibbs energy change: all components in standard state = pure

A low (very negative) ΔG means strong reaction to the right, i.e. a high equilibrium constant:

$$K = [MO_2] / [M]\ pO_2$$

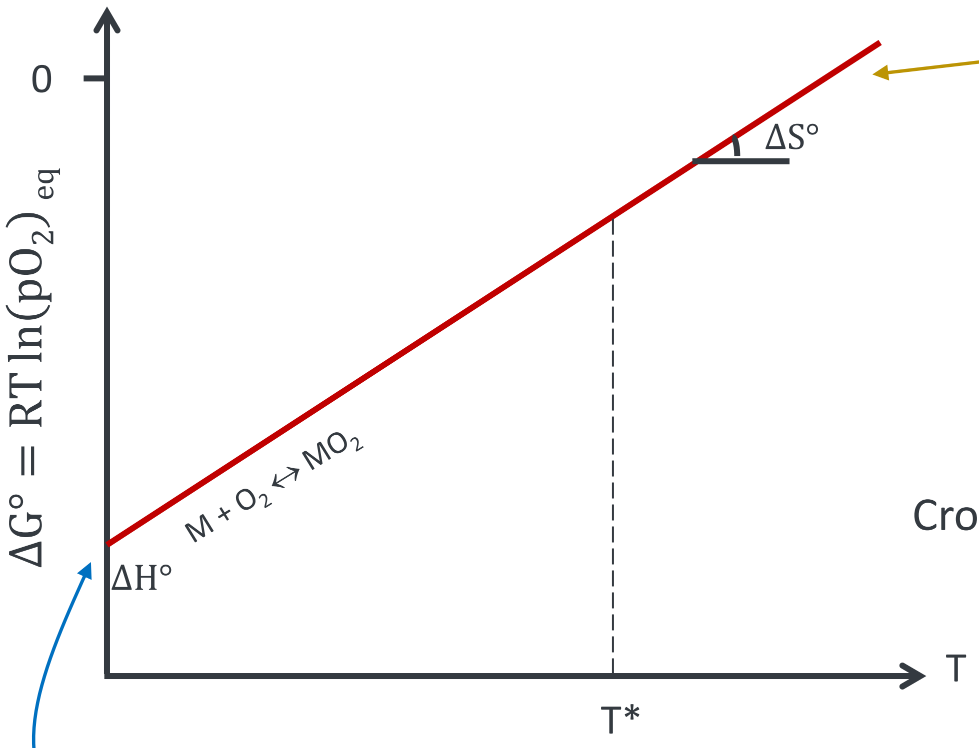
Where [] indicates the activity ("concentration") of the component in case of a mixture (gas, slag,…)

By measuring **pO_2** with pure metals/oxides, ΔG can be derived



Plotting standard reaction Gibbs energy

- Graphical view: $\Delta G° = f(T)$



Slope of the line

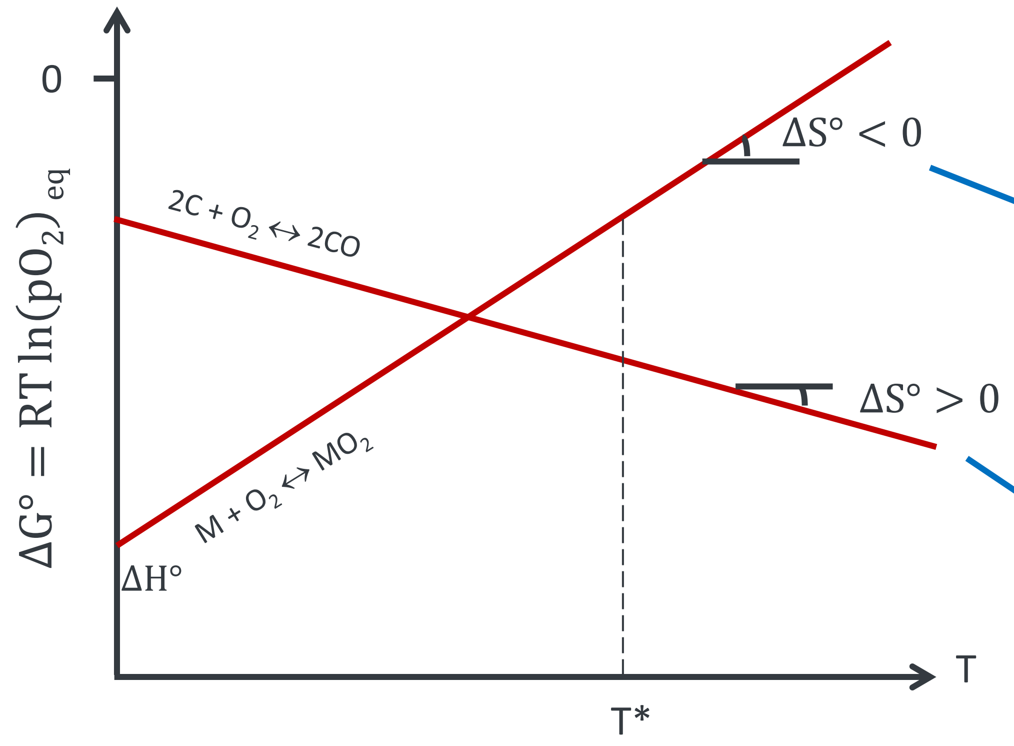
$$\boxed{\Delta G° = \Delta H° - T\Delta S°}$$

Crosses the Y axis (T=0)

= Reaction heat

Visualization – Reactions

- Graphical view: $\Delta G° = RT \ln(p_{O2})_{eq} = f(T)$



$$\boxed{\Delta G° = \Delta H° - T\Delta S°}$$

$\Delta S° < 0$
Typical for metal oxidation
Consumption of O_2 gas = reduction of entropy

$\Delta S° > 0$
Carbon oxidation
Production of CO gas = increase of entropy

Ellingham diagram

Oxidation reactions

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= RT\ln(pO_2)_{eq}$$

Always for reaction with 1 mole of O_2

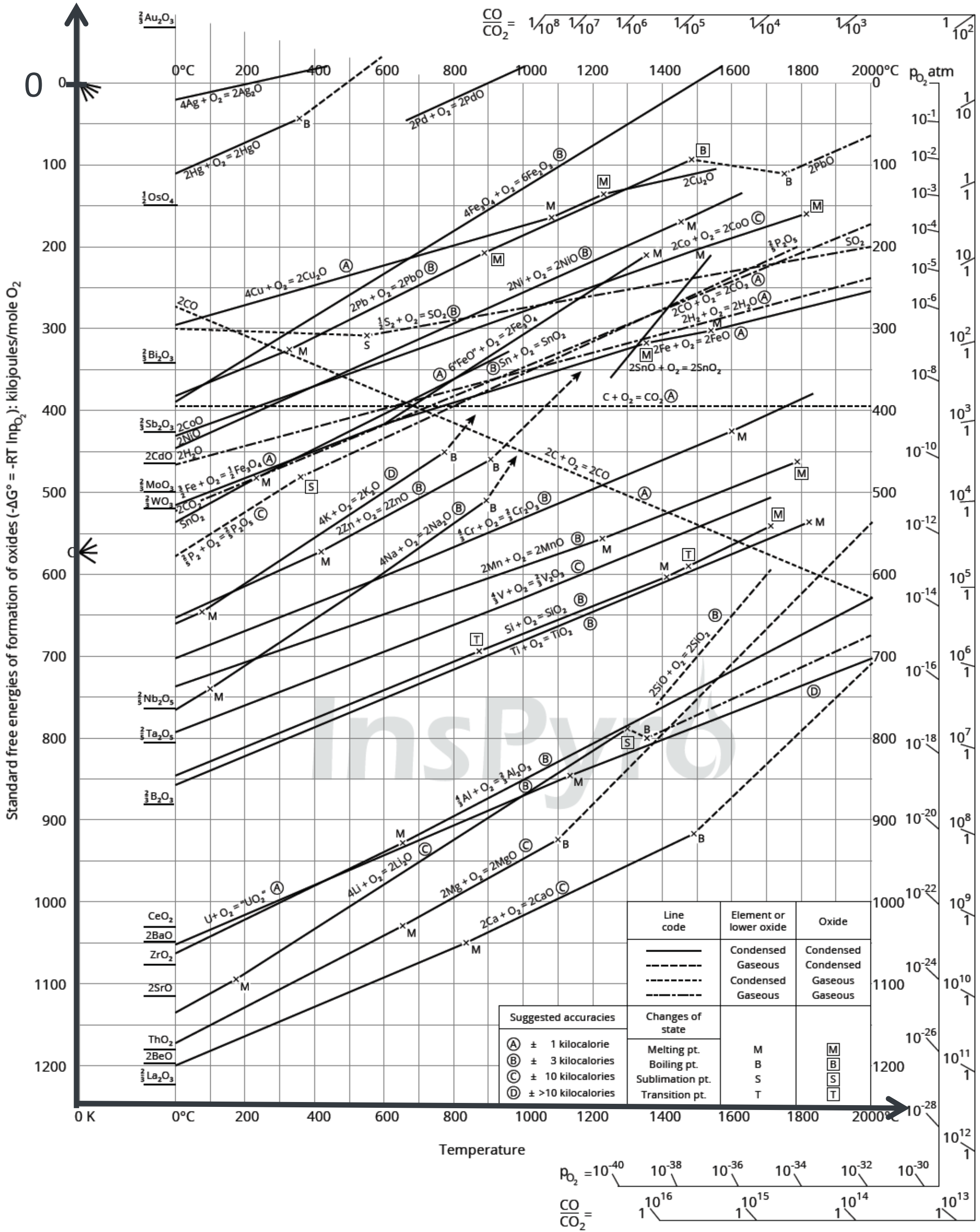
Always for pure compounds

“Competition” for oxygen,

compare stabilities of:

- Oxides from different metals
- Different oxidation states of single metal

High T → metal oxides less stable



Line code	Element or lower oxide	Oxide
———	Condensed	Condensed
– – – –	Gaseous	Condensed
- - - - -	Condensed	Gaseous
–·–·–·	Gaseous	Gaseous

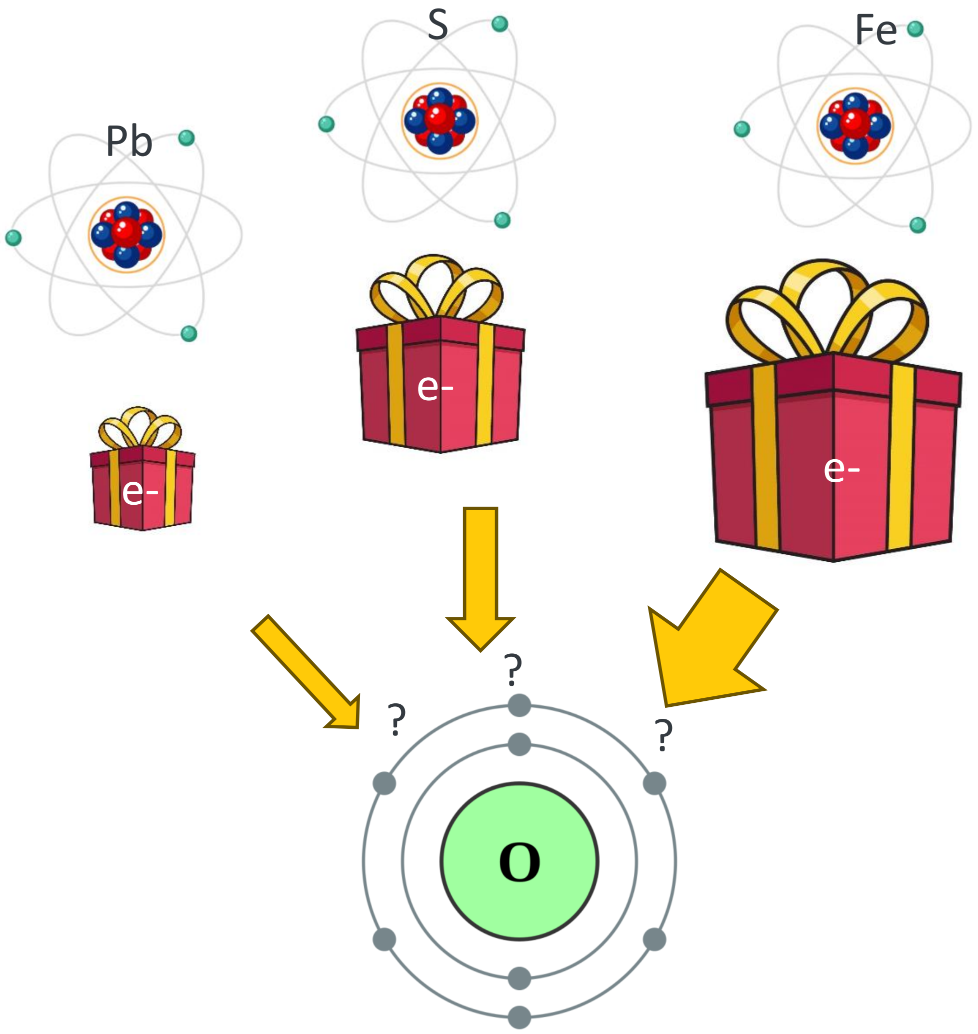
Changes of state	Element	Oxide
Melting pt.	M	M
Boiling pt.	B	B
Sublimation pt.	S	S
Transition pt.	T	T

Suggested accuracies
Ⓐ ± 1 kilocalorie
Ⓑ ± 3 kilocalories
Ⓒ ± 10 kilocalories
Ⓓ ± >10 kilocalories

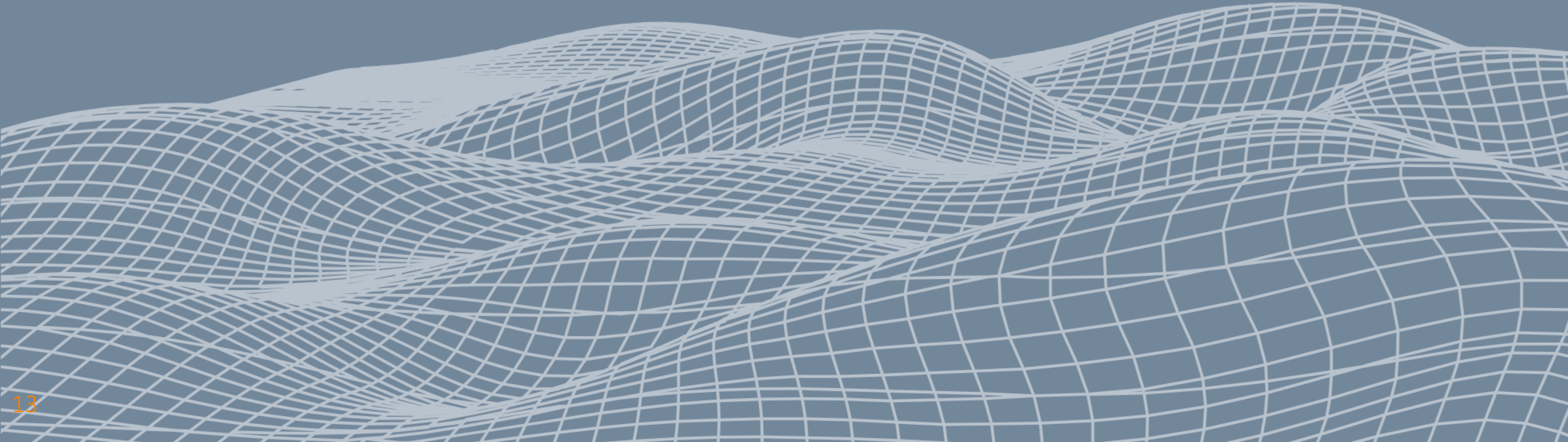
=> inspyro.be

Competition for oxygen

- $M_1, M_2, M_3 + O_2 \Rightarrow M_?O$
- Oxygen can only bind once, so it has to choose
- Metals that will win are the ones with:
  - Lowest DG°
    - Direct energy from forming oxide (~Electronegativity)
    - See Ellingham diagram
  - Lowest activity for oxide
    - A sink for the oxide, pulling it in the slag
  - Highest activity for metal
    - Pushing the metal out of the alloy



Lead metallurgy basics



Primary vs. secondary lead smelting

Primary

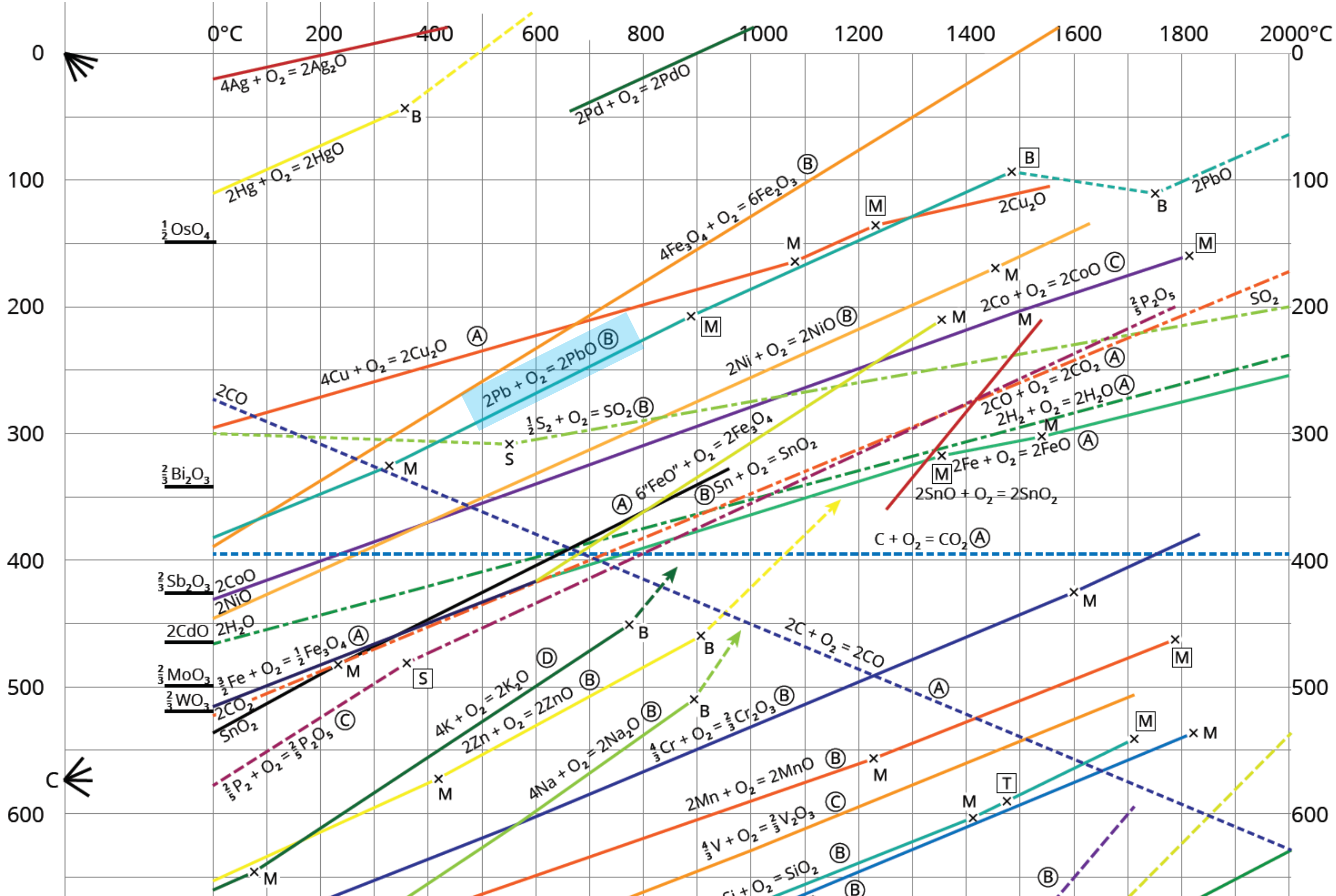
- Raw material: concentrates
  - Fine powder
  - Well-known composition
  - Blending
- Chemistry: Sulfides
  - Oxidize = Exothermic reaction

Secondary

- Batteries (etc.)
  - Different sizes
  - Seasonal fluctuations
  - Organics
- Metallic, oxides, sulfates
  - Reduce = Endothermic reaction

Very different starting points – so different routes – but same theory as Pb is still Pb

Ellingham diagram: lead smelting



InsPyro

Ellingham: oxidation preference

- Lead is relatively noble
- In the lead smelting range:
  - Fe could be FeO or Fe_3O_4
  - Sb, Sn, Ni can be oxidized
  - S can be oxidized
  - Bi, Cu, Ag stay metallic
  - C can reduce all of the above
  - Typical slag elements Si, Al, Ca, etc. definitely oxidized

- This is a rough approach, as dilution may influence the result
  - E.g. Sb diluted in Pb: not possible to oxidize all Sb without oxidizing some Pb
  - E.g. Pb in slag: thermodynamic equilibrium concentration of PbO is never 0

Predominance diagrams

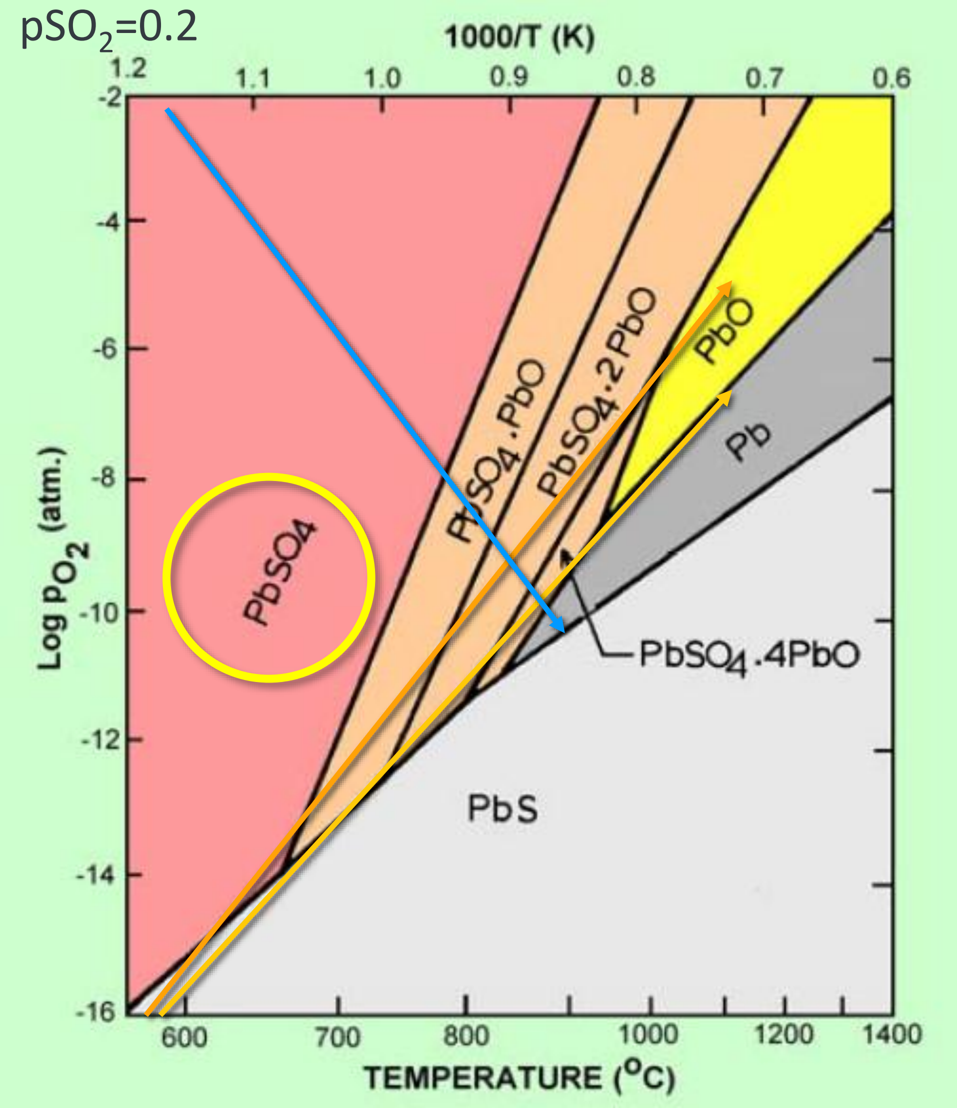
- Ellingham gives a good idea about what oxidizes first
- When sulfur comes into play, elements can choose between
    - Metallic form
    - Oxide form
    - Sulfide form
    - Sulfate form

=> Need a different diagram to understand what happens in which condition

Lead predominance diagram

- Sulfate very stable at low T
  - SO_2 to gas phase upon heating in air
- Classical sintering
- Direct smelting
- Recycling

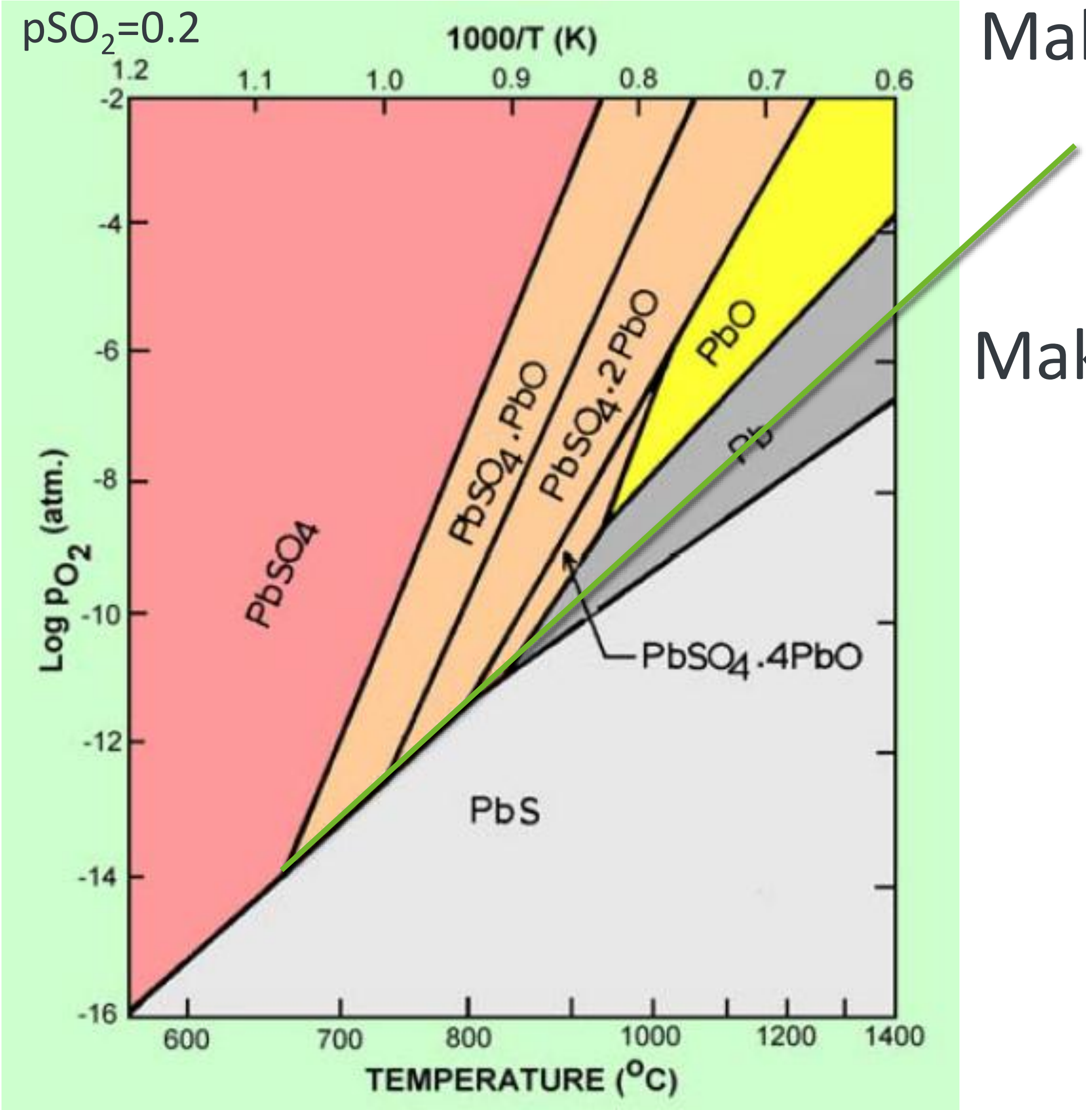
- Different challenges!



Graph D. Swinbourne, RMIT

Lead predominance diagram

- S challenge in lead recycling:
  - Oxidizing atmosphere: make PbO and SO_2
  - Reducing atmosphere: make PbS
- This diagram is too simple, with pure compounds only…



Make SO_2

Make PbS

Graph D. Swinbourne, RMIT

Yazawa diagram for Pb

pO_2-pS_2 diagram with solutions

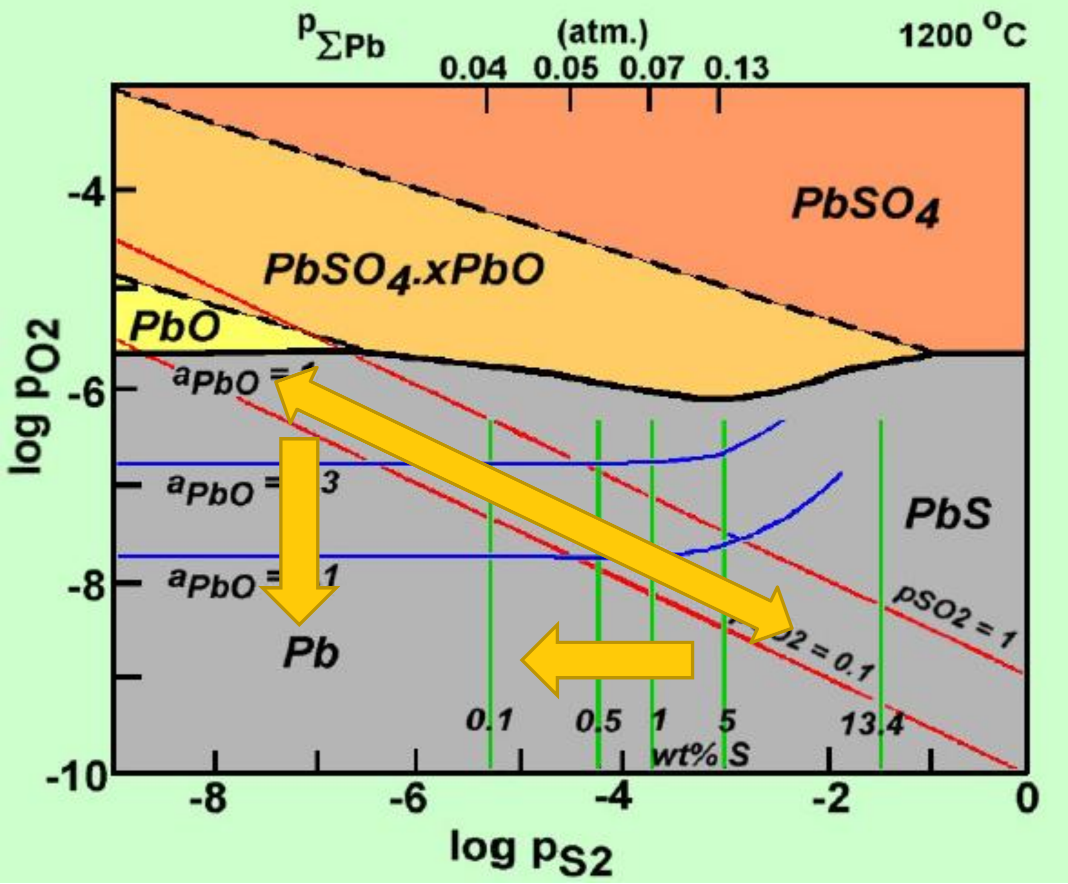
- Pb-PbS continuous (bullion-matte)
- PbO diluted in slag (silicate or soda slag/matte)
- Choose high PbO or high PbS!

Metallurgical strategies:

- Remove SO_2 first, then reduce PbO to Pb
  - Paste desulfurization (pre-de-S)
  - Roasting/dissociation in furnace (post de-S)
- Reduce to PbS , then make Pb using a sulfur capturing flux, Fe or Na_2CO_3

More Pb to gas →

More PbO in slag



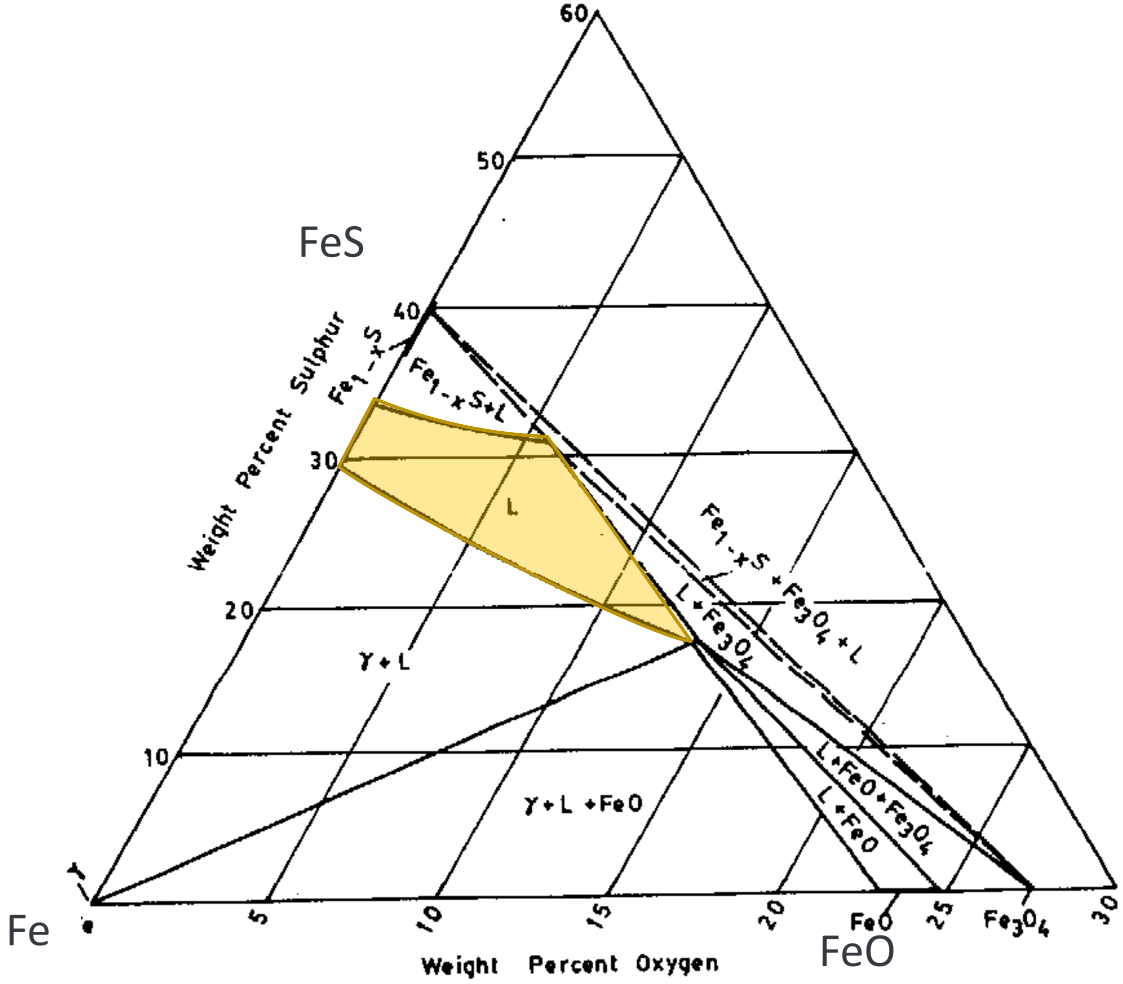
More S in bullion

Graph D. Swinbourne, RMIT

Fluxing making the system quite complex…

- S captured in slag => FeS, Na_2S, formation
    - Slags with a lot of S should rather be called mattes!
- When not reducing well, also FeO, Fe_3O_4, or Na_2SO_4 forms
    - FeO and Na_2SO_4 dissolve well in sulfide system, Fe_3O_4 not
- Other elements such as SiO_2 and CaO present
    - SiO_2 does not like sulfides so may lead to a slag-matte separation

Some relevant diagrams for matte/slag…



35.5b Fe-O-S Isothermal Section at 1100°C in Weight Percent

Raghavan 1988 (compilation)

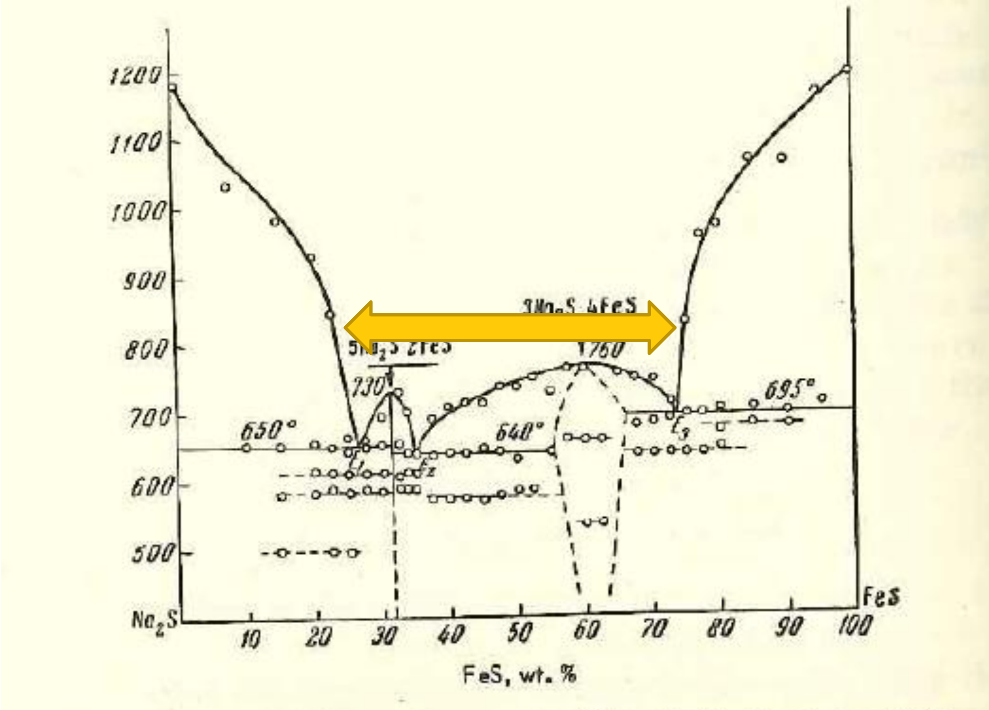
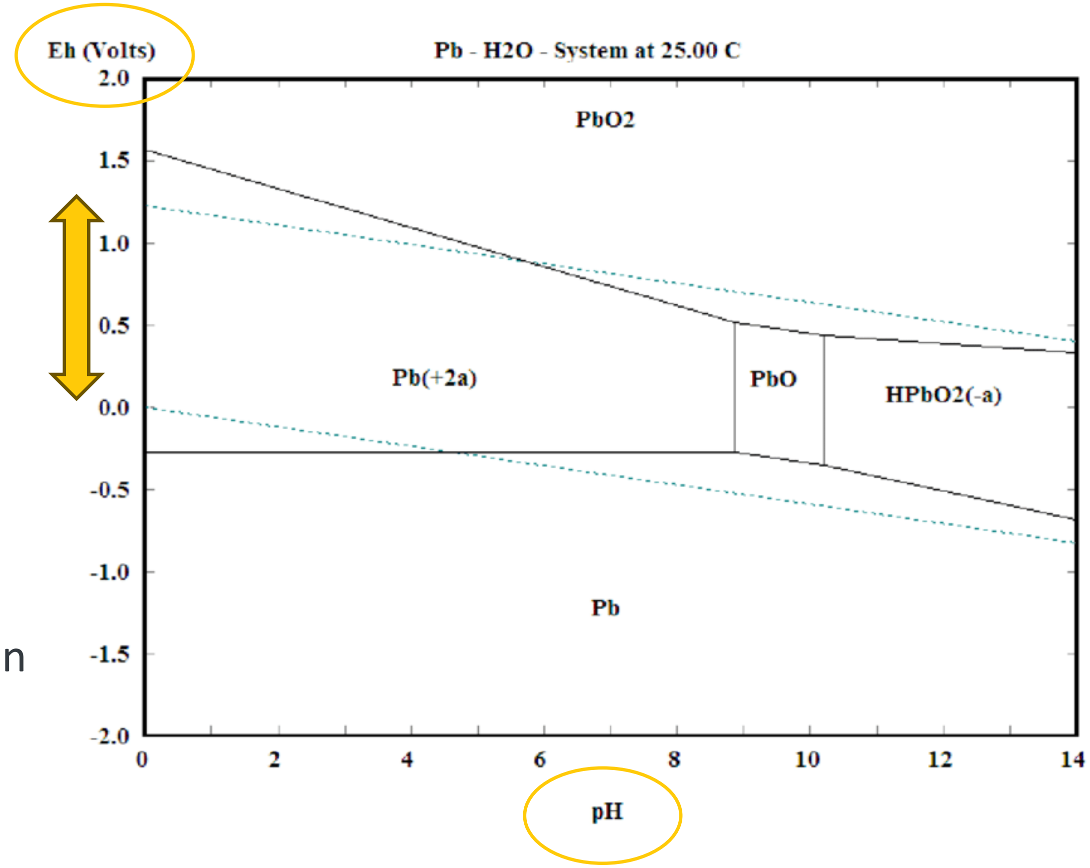


Fig. 2. Equilibrium diagram of the FeS–Na_2S system.

N. Kopylov, the Cu_2S-FeS-Na_2S system, 1964

Lead hydro – E-pH diagram

- E-pH or Pourbaix diagram: showing the stable phases/ions in aqueous conditions



O_2 formation

Water stability region

H_2 formation

Theoretically…
We can bring Pb into solution
We can deposit it as metal

Simulate. Quantify. Optimize.

Redox equilibrium

- The standard electrode potential of a reaction is written as E^0
  - $Metal^{z+} + z\ e^- \leftrightarrow Metal$ $E^0 = \ldots$ V
- Standard conditions:
  - 1 atm
  - 25°C
  - a=1
- Can be calculated from/to thermodynamics: Gibbs energy
- $E^0 = \frac{-\Delta G}{zF}$
  - ΔG = Gibbs free energy change
  - z = number of electrons
  - F = 98485 Coulomb/mol (Faraday constant)
- Spontaneous reaction if DG<0 => if E>0
  - Relevant for two combined half reactions

Ellingham diagram: p_{O2} indicator of DG
Pourbaix diagram: E° indicator of DG

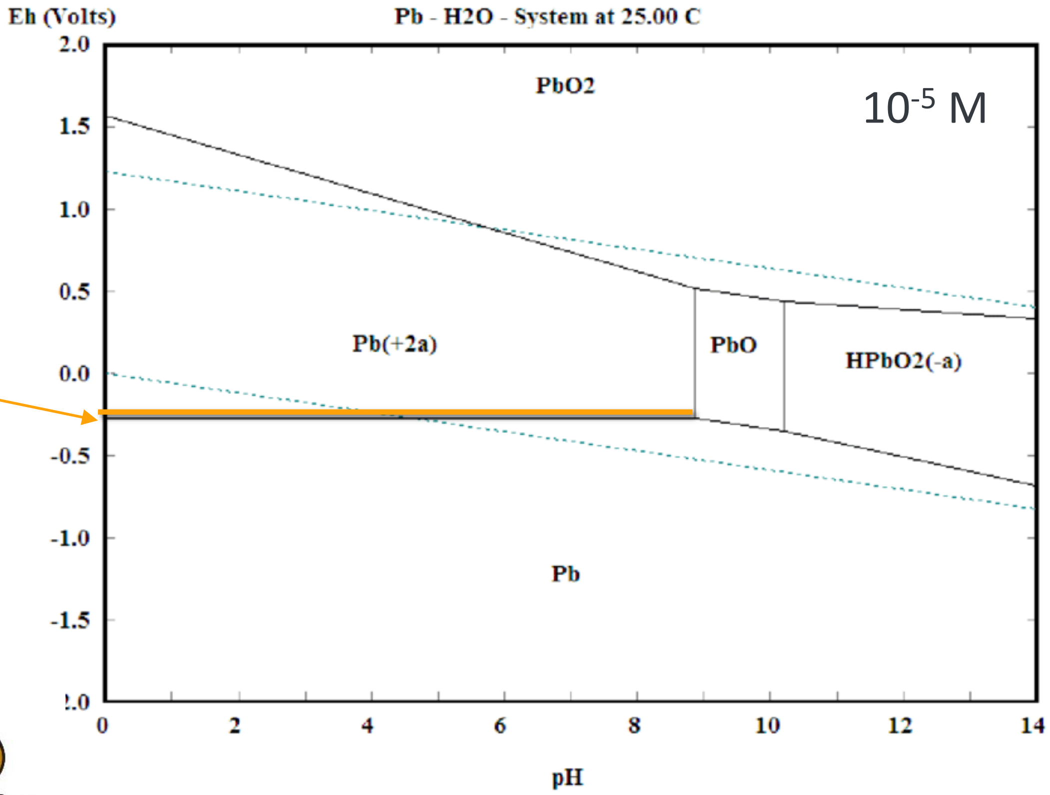
Redox potential

More noble
(mostly as metal)
Low DG

Less noble
(Mostly as oxide/salt)
High negative DG

Metal/metal ion equilibrium	E^0 vs. H_2/H^+ [V
Au/Au^{3+}	+1.498
Pt/Pt^{2+}	+1.2
Pd/Pd^{2+}	+0.987
Ag/Ag^{+}	+0.799
Hg/Hg^{2+}	+0.788
Cu/Cu^{2+}	+0.337
H_2/H^+	0.000
Pb/Pb^{2+}	-0.126
Sn/Sn^{2+}	-0.136
Ni/Ni^{2+}	-0.250
Co/Co^{2+}	-0.277
Fe/Fe^{2+}	-0.440
Cr/Cr^{2+}	-0.744
Zn/Zn^{2+}	-0.763
Al/Al^{3+}	-1.662
Mg/Mg^{2+}	-2.363
Na/Na^{+}	-2.714
K/K^{+}	-2.925

Dissolved metal conc. 1M

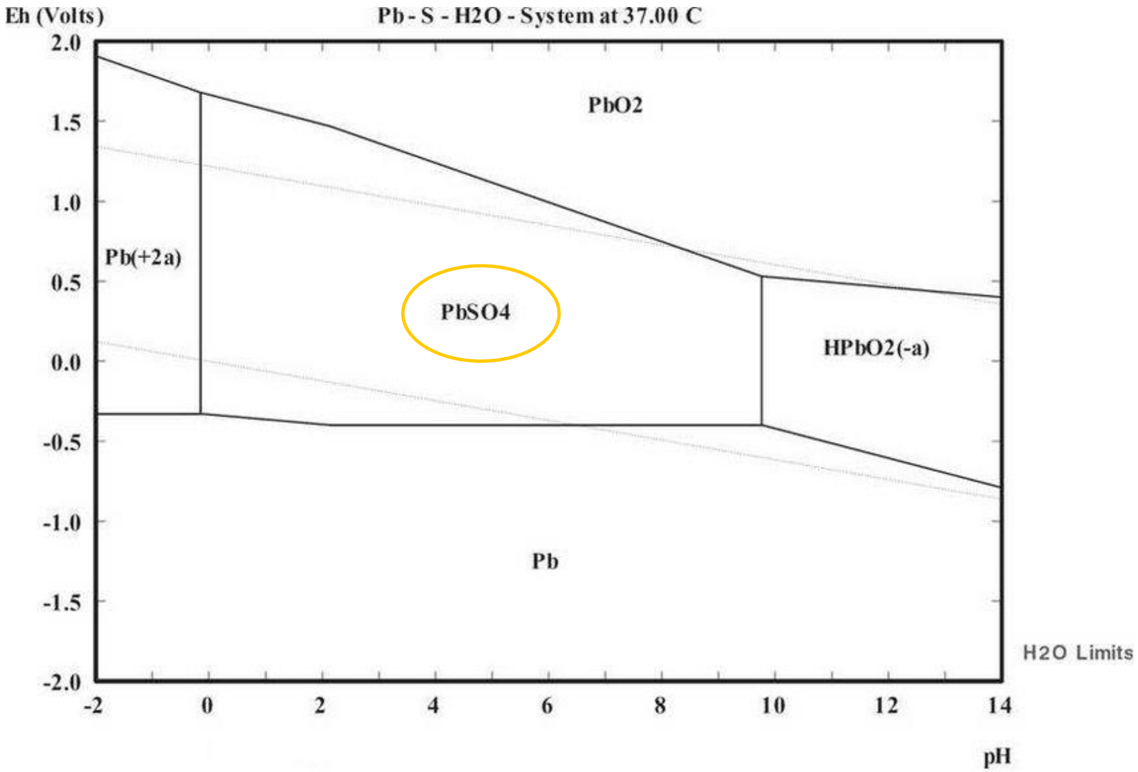


Competition for giving away electrons! Most base metals >Pb

Simulate. Quantify. Optimize.

Lead E-pH diagram

- Pb sulfate very stable: cannot be dissolved in common conditions
- Need to remove sulfate and replace with another anion

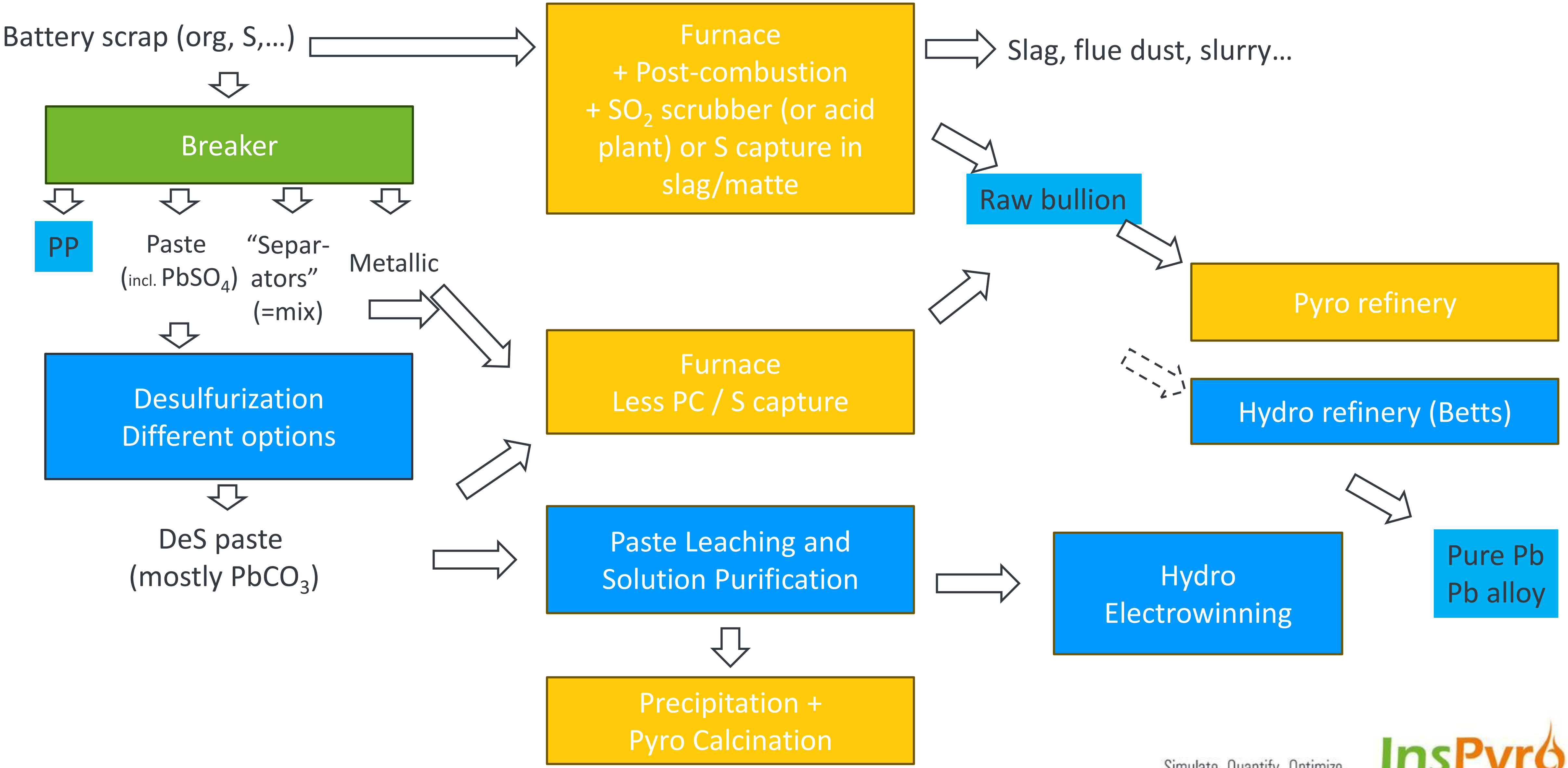


Pb desulfurization:

- Bring SO_4 into solution, e.g. Na_2SO_4
- Pb stays solid as $PbCO_3$ or $Pb(OH)_2$

Pb leaching needs a next step at lower pH

Lead recycling routes



Battery scrap (org, S,…)

Breaker

PP

Paste (incl. $PbSO_4$)

"Separators" (=mix)

Metallic

Desulfurization
Different options

DeS paste
(mostly $PbCO_3$)

Furnace
+ Post-combustion
+ SO_2 scrubber (or acid plant) or S capture in slag/matte

Slag, flue dust, slurry…

Raw bullion

Furnace
Less PC / S capture

Paste Leaching and Solution Purification

Precipitation +
Pyro Calcination

Hydro
Electrowinning

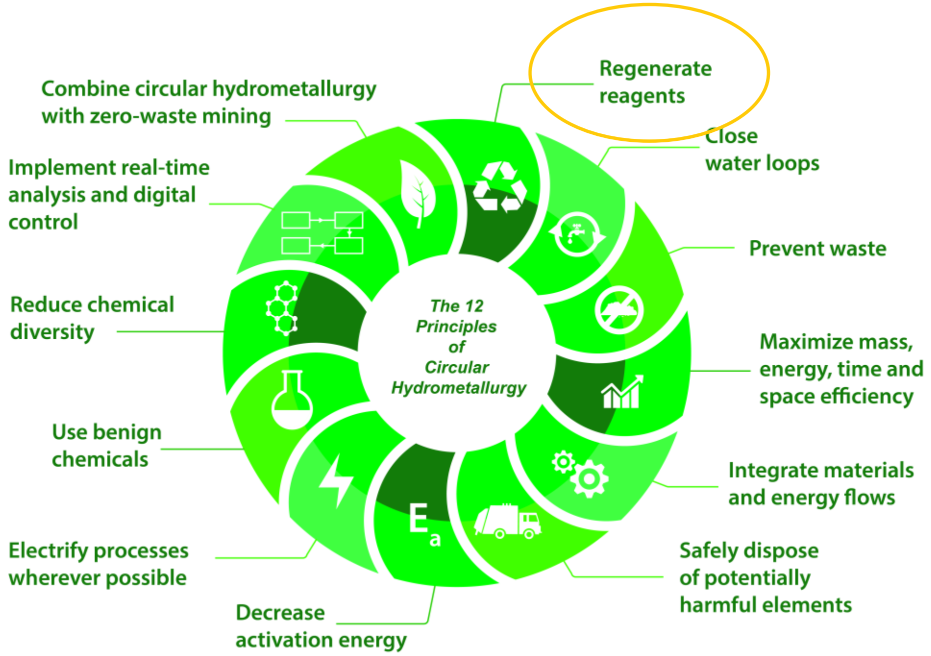
Pyro refinery

Hydro refinery (Betts)

Pure Pb
Pb alloy

Lead hydro – Getting lead out of the solution

- Electrowinning
  - Product depends on the medium
  - Fluoroboric acid (Betts): High purity plating
  - Ammonium chloride: metal flakes
  - MSA, alkaline processes: spongy metal
- Precipitation
  - Precipitate depends on the solute (direct use as powder?)
  - Use of organic acids (citric acid, acetic acid): precipitates can be calcined to PbO
  - “Hydro process without acid recovery is not circular”
- **New ideas**:
  - Solid paste reduction (avoid leaching - spongy)
  - Two-chamber electrolysis (separated by membrane)



The Twelve Principles of Circular Hydrometallurgy,
K. Binnemans, P.T. Jones, 2023
https://doi.org/10.1007/s40831-022-00636-3

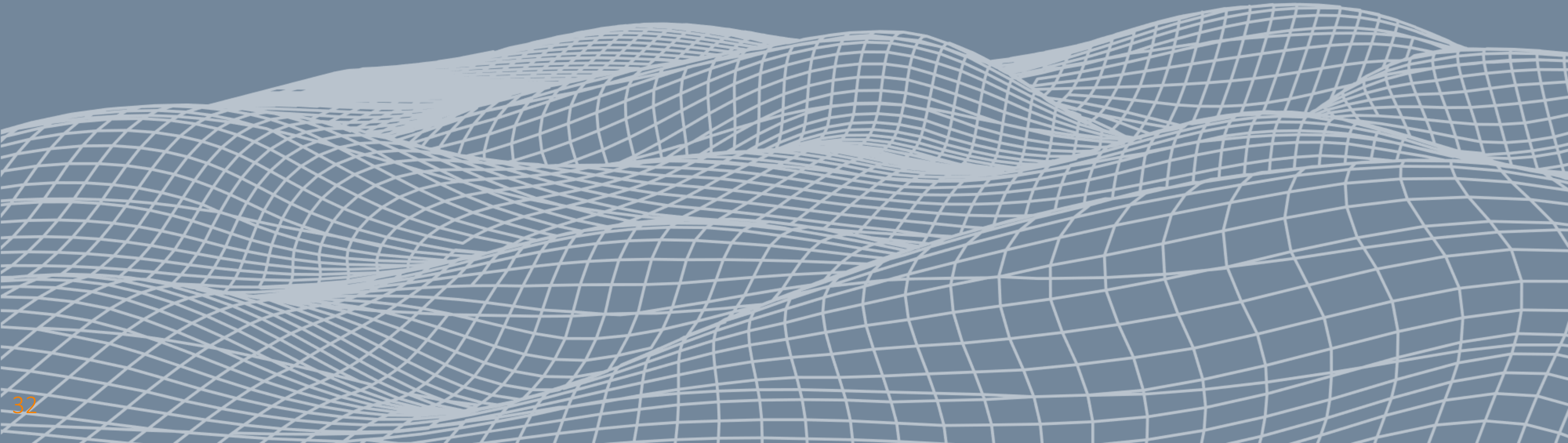
Pyro – Hydro

- Pyro good at:
  - Making a useful alloy with few steps
  - Robust towards impurities
  - Get rid of organics, shapes, mixes
  - Typically, slag as “single” outlet (but challenges with Pb and variable matte/slag system)
- Hydro good at:
  - Making a very pure metal (Betts refining)
  - Low dust levels
  - Removing S from paste, solutions and gases
  - Typically, selectivity (but for lead, limited options for selective leaching)
  - Typically, precipitating and crystallizing pure products (salts, hydroxides)
  - Typically, good combination with electrification (=> reagent recovery) – will we see an electrolysis solution for Pb?
- All starts with good mechanical separation
- Combine technology to use their strengths

Next frontiers

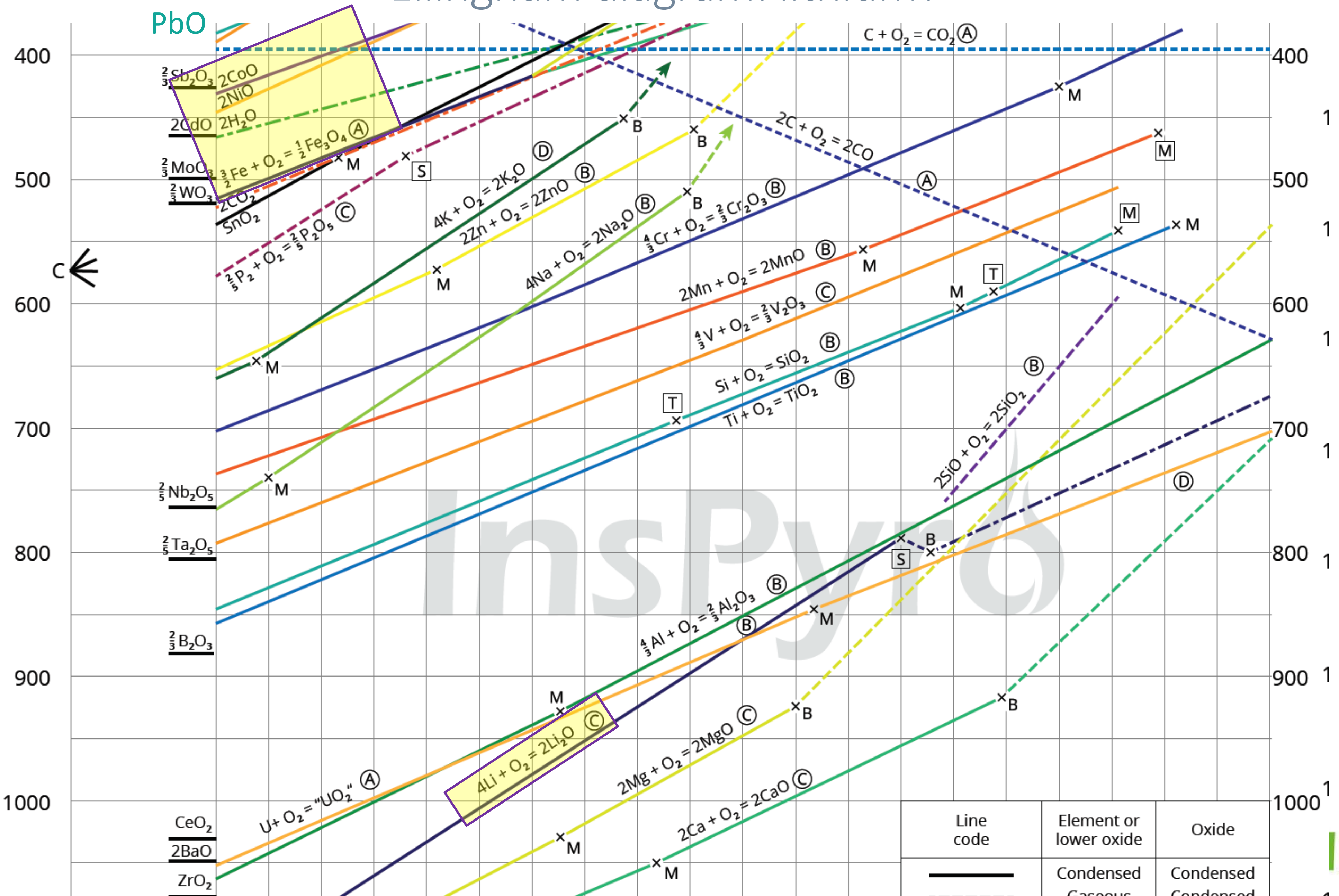
- Zero waste
  - Pyro: slag and/or filter dust as the waste bucket… But not a useful outlet
    - Efforts to fume out Pb and Zn and reach a building quality slag – but hard
    - Needs scale. E.g. integration with Zn flowsheets
    - Hydro cannot help on slag, creates more leach residue which is a very poor building material
  - Hydro towards zero waste: different waste bucket depending on process, limited attention to impurities
- Recovery of trace elements
  - Pyro: in alloy / via refinery, rest lost to slag – attention depends on price
  - Hydro: increases complexity, but impurities need outlet
- CO_2 emissions reduction
  - Pyro: Reduction with hydrogen/biomass? Make green H_2 or electrolyze Pb instead? Biomass availability?
  - Hydro: Direct electrification, reagents footprint

Lithium metallurgy basics



Ellingham diagram: lithium?

PbO

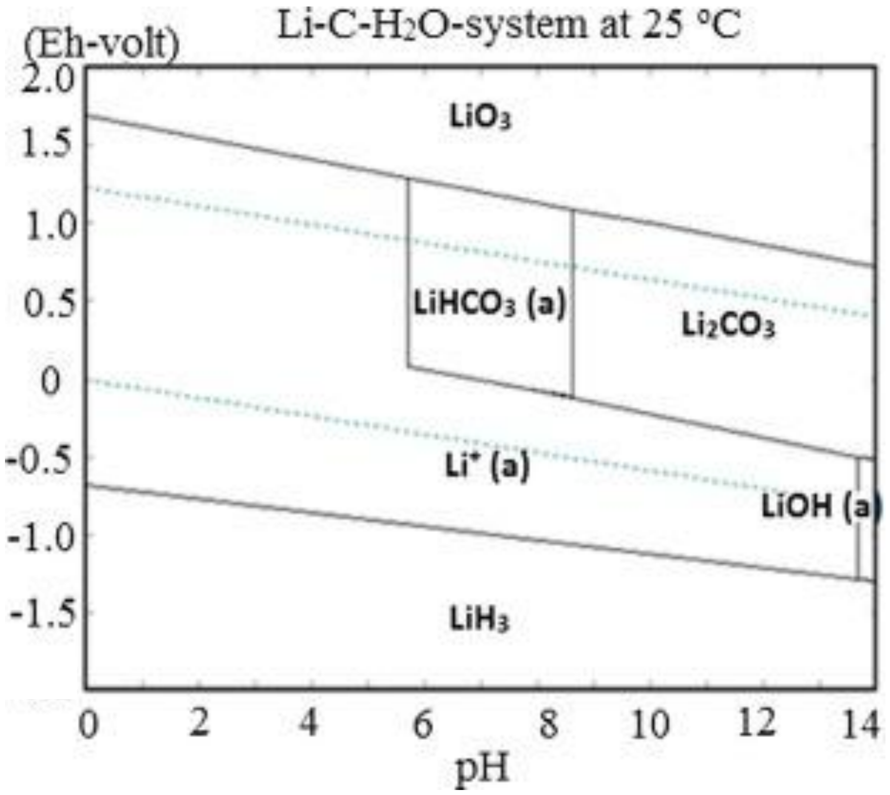


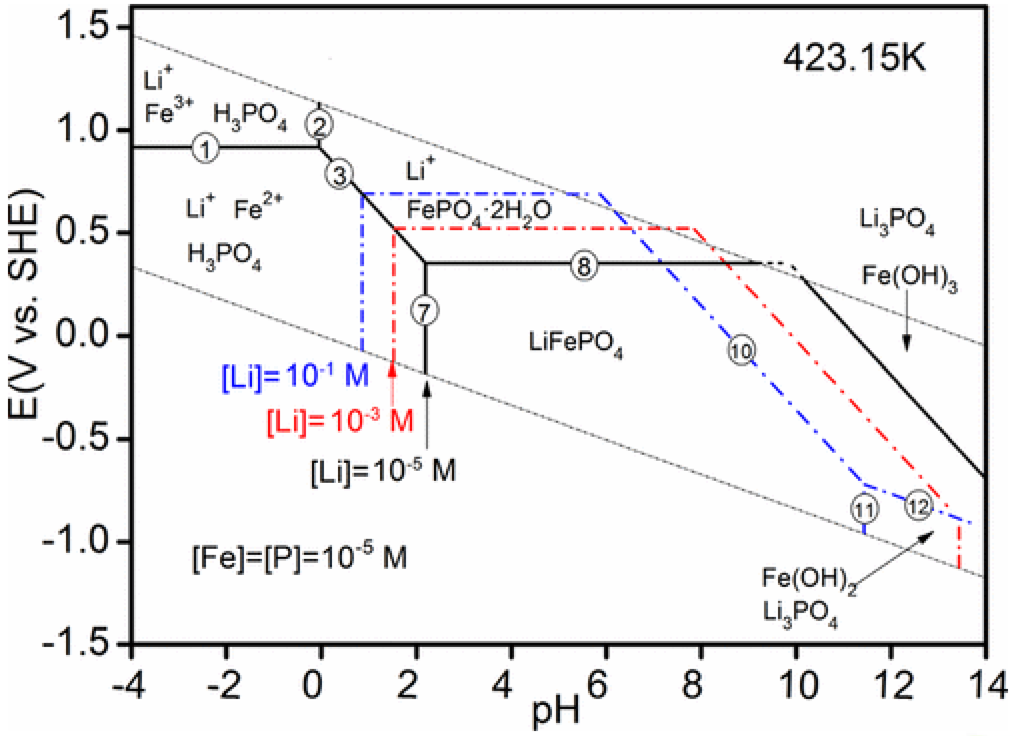
Li pyro: Ellingham

- Li very low in the diagram
  - Will be one of the last to be reduced – not possible using C or even Al
  - In practice, will not (+does not need to) be reduced
  - Making metal not necessary, active materials contain Li as oxide/salt
  - Except for Li metal batteries – molten salt reduction, not in scope today
- Compare to Pb:
  - Ca/Si/Mg/Al oxides, fluxes, etc. will be in the slag
- With pyro on LIB's:
  - Rather noble elements (Cu, Ni…) can be recovered in alloy
  - Li will be part of the slag, along with any common slag forming impurities
  - => Additional steps needed to recover it

Li hydro: E-pH diagram

- Li very soluble, in several salts
- Bound/intercalated in an oxide depending on other elements present (LFP, NMC…)
  - To be reversed for recycling
- No Li metal in aqueous system either





Li metal E°=-3V

Primary vs. secondary Li flowsheets

Primary

- Raw material: concentrates
  - Well-known composition
  - Mine dependent
- Chemistry: Rocks (oxides) and brines (salt)
  - Rocks need treatment to make Li soluble
  - Li in brines needs separation from other salts

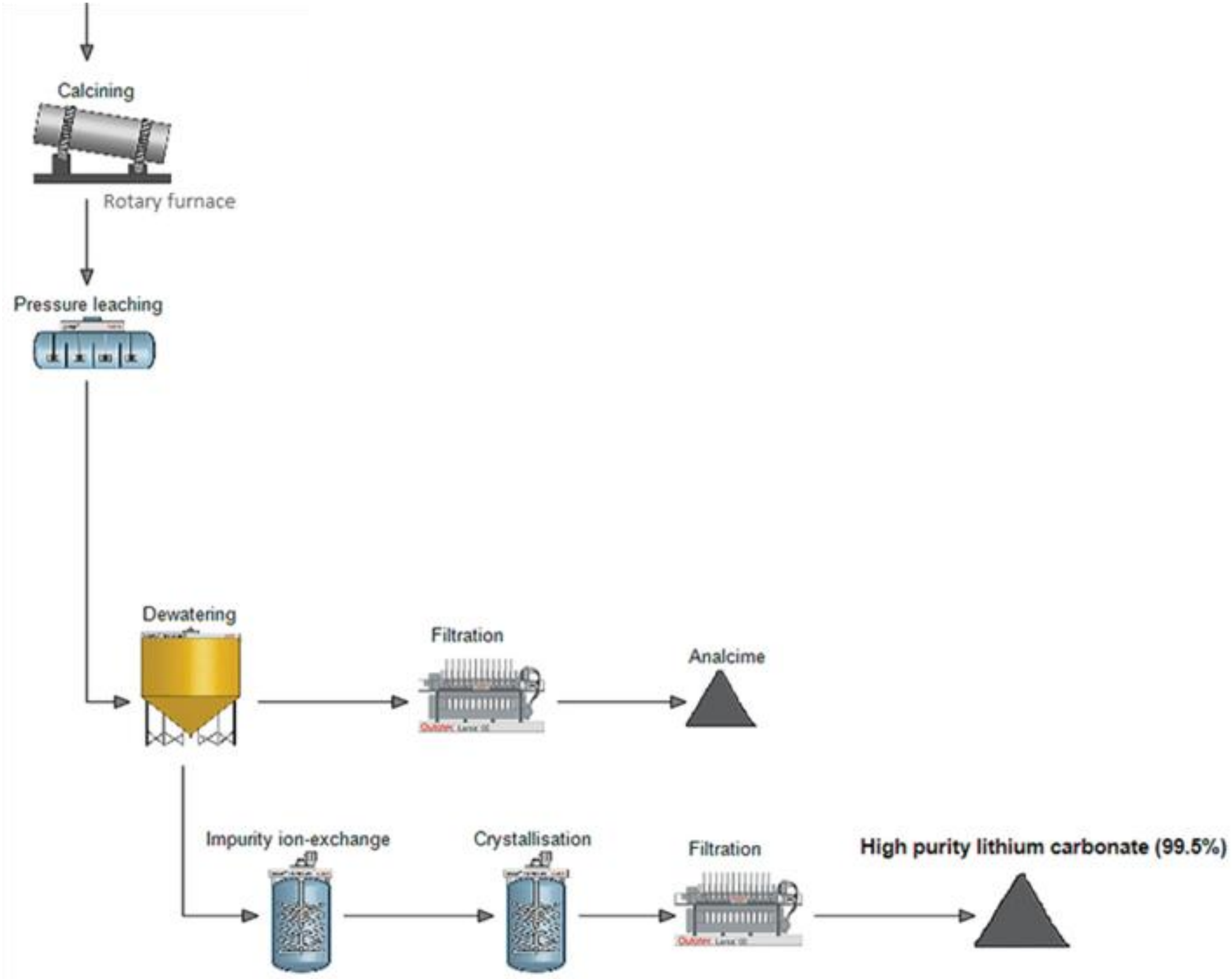
Secondary

- Batteries / black mass
  - Different chemistries
  - Evolution as chemistry evolves
  - Organics
- Li in lithiated oxides / graphite
  - Li strongly bound in active material
  - Pretreatment and leaching to bring into solution

Different starting points – some comparison possible (Li is Li)

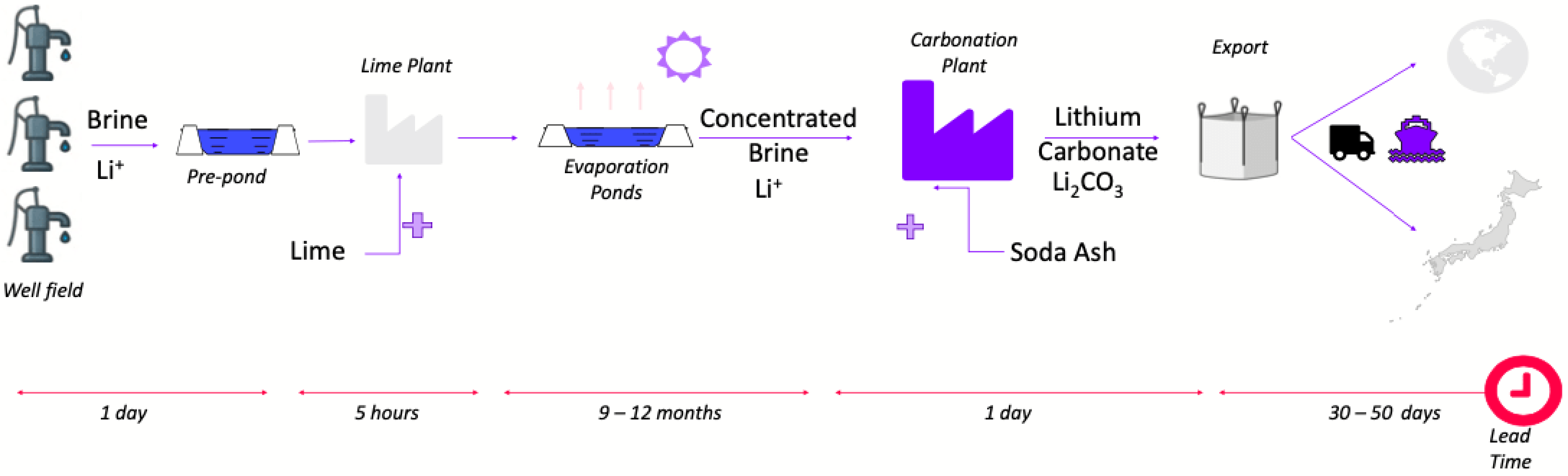
Li_2CO_3 production from hard rock concentrates

- Calcining at 900-1100°C
  - Transform spodumene $LiAl(SiO_3)_2$ crystal structure
- Autoclave leaching with Na_2CO_3
  - Alternatively roasting 200-300°C +water leaching
- Impurity removal from leach solution
- Carbonization ($LiHCO_3$)
- Crystallization of Li_2CO_3
  - Next step can be conversion to LiOH with $Ca(OH)_2$
  - Alternative route for LiOH is through Li_2SO_4 with H_2SO_4 then NaOH



Kokkola plant DOI: 10.13140/RG.2.2.20597.22243

Li_2CO_3 production from brines

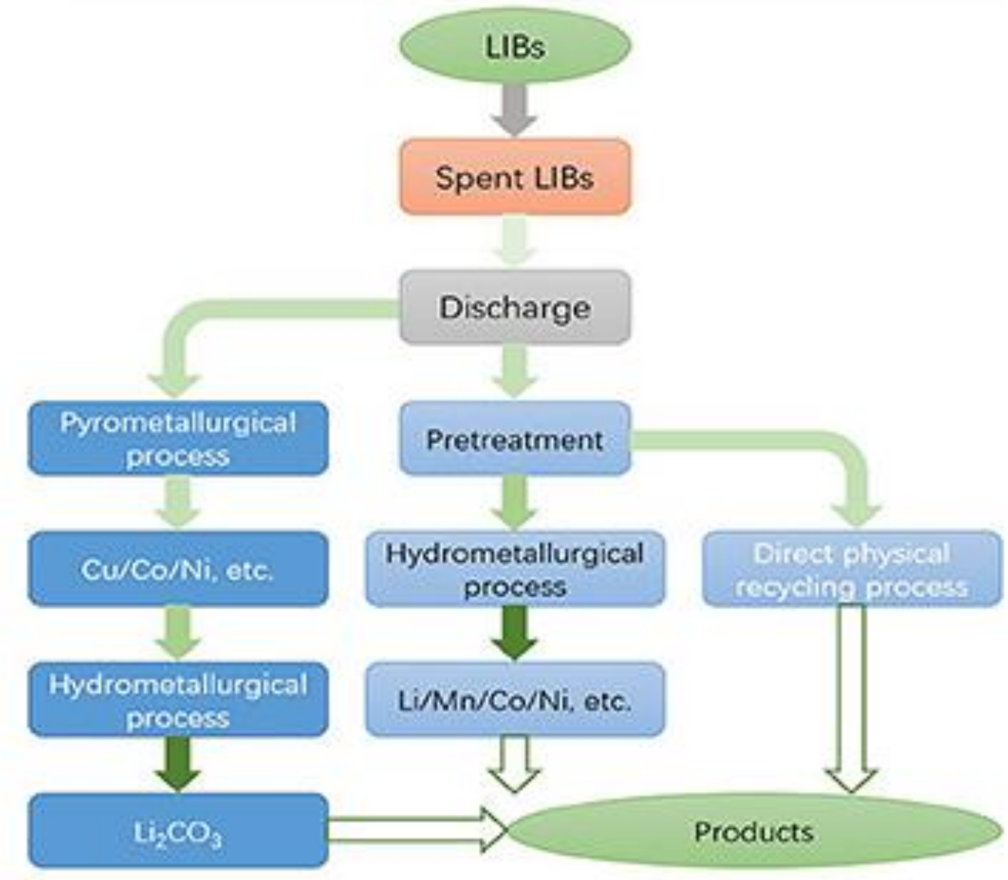


Wells	Lime Plant	Ponds	Carbonation Plant	Logistics
Brine extraction from the Olaroz basin	Elimination of Mg from the brine	Solar evaporation increases brine concentration while precipitating salts though	Carbonation reaction to obtain Lithium Carbonate with impurity removal	Packing the final product into 1 tonne bags for export

https://stockhead.com.au/

Li-ion battery recycling

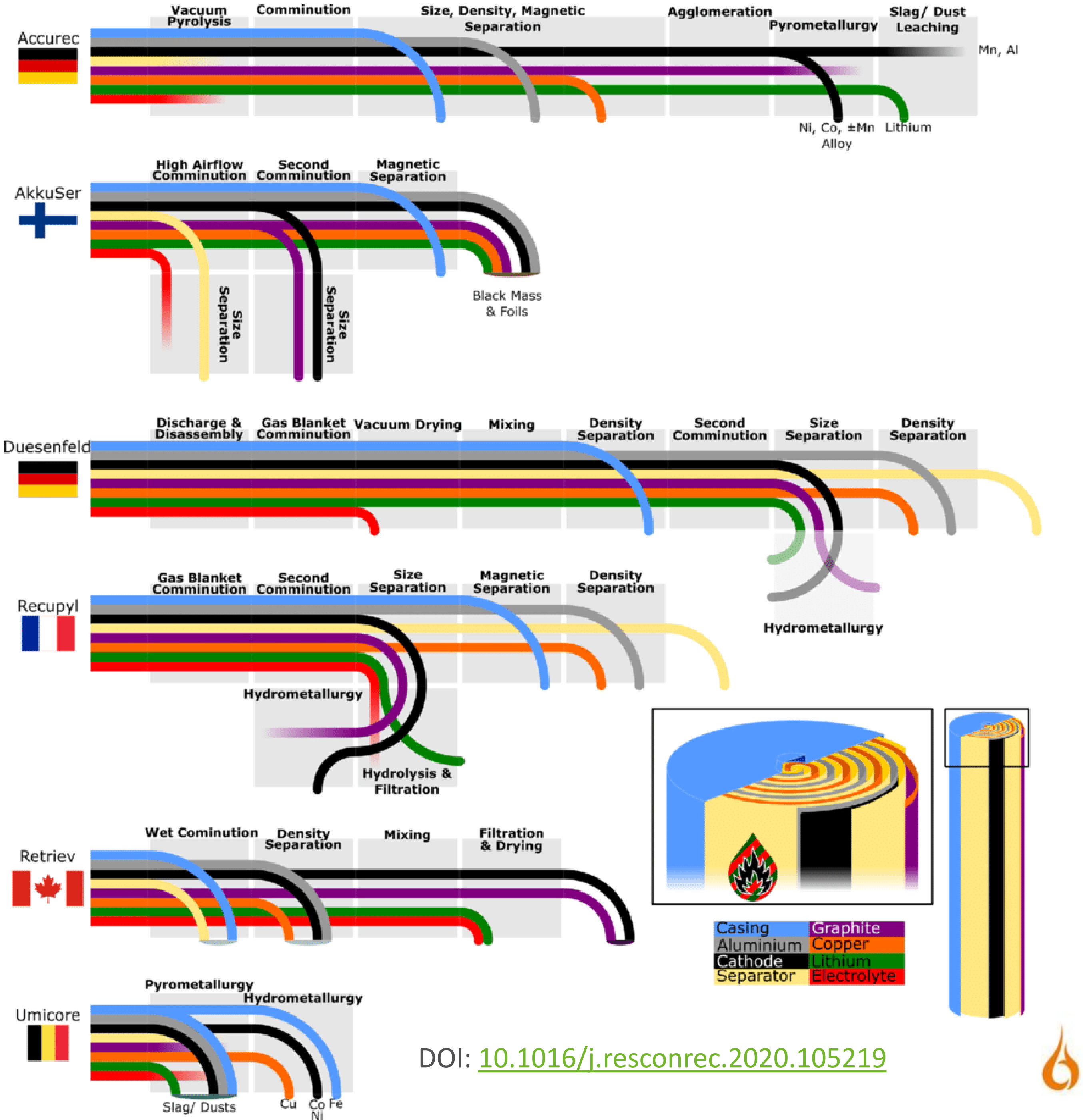
- … is **not** only **about Li**!
- General approaches
  - Mechanical separation
    - Basic materials (plastic, Fe, Al,…) + black mass
    - Possibly split black mass in components (direct physical recycling)
  - Pyrometallurgy
    - Recover Cu/Co/Ni/Fe in alloy
    - Some options to recover Li…
  - Hydrometallurgy
    - Leaching of black mass (or pyro alloy)
    - Precipitation of active materials (CAM)



https://www.frontiersin.org/articles/10.3389/fchem.2020.578044/full

LIB recycling

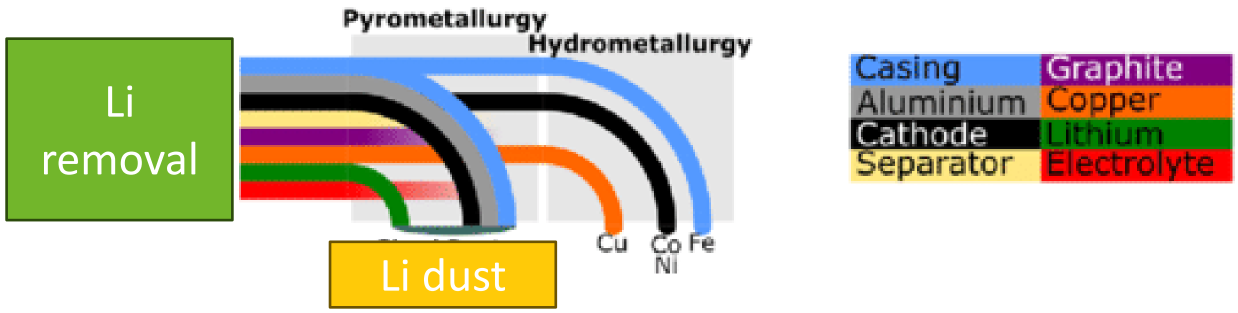
- 2020 Sommerville paper gives collection of (Western) techniques
- Their assessment:
  - No industrial standard process yet
  - Try to recover more than only the most valuable materials
  - Automation of disassembly needed
  - Mechanical separation and direct reuse favourable
- Our assessment:
  - Lots of evolution since then
  - Combine techniques for what they are good at
  - Recoveries improving and more focus on other materials (Li, graphite…)



DOI: 10.1016/j.resconrec.2020.105219

Li recycling

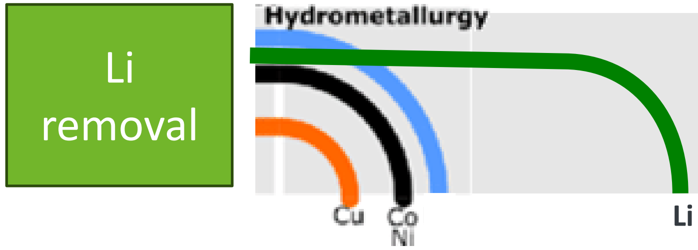
- Classical pyro approach:
  - Smelt batteries – now rather black mass
  - Retrieve metals in an alloy
  - Reactive Li reports to the slag, diluted


Li removal

Li dust

- Classical hydro: leach all, precipitate base metals, recover Li at the end

Black mass


Li removal

- Pyro optimization: fume Li to flue dust (less volume with higher Li concentration) e.g. by addition of $CaCl_2$

Li recycling

- Lithium removal first: make Li more soluble and leach it out, several methods:
  - Reductive (carbonation) roasting (also: pyrolysis)
  - Hydrogen reduction
  - Sulfation roasting
  - Leaching directly (oxidative, e.g. for LFP, or reductive) – but easier to deal with organic content with at least one thermal treatment step
- Why is "lithium first" on the rise?
  - Higher yields: focused conditions for Li removal, no losses in subsequent steps
    - Li now a relevant part of the value, esp. for LFP
  - Combines well with pyro (avoiding low yields)
  - … but essentially gives the freedom to choose the next steps as fit, depending on e.g. available volume
    - Pyro requiring higher volume
    - Hydro as transition / for smaller markets

Next frontiers

- Zero waste – reagent recovery
  - Salt splitting: Na_2SO_4 to NaOH and H_2SO_4
  - May become required as salt discharge is not allowed
  - Technically possible, but challenging economics

- Total recycling – recovery of more than metals, back to battery materials
  - Electrolyte
  - Graphite

- Recycling as a geopolitical security strategy

Some conclusions

- Lead flowsheets
  - Sulfur is the key
  - Robust established flowsheets, no revolution needed but innovation welcome
  - Local recycling, not gigarecyclers
  - Can we get better at separation? What about separators/heavy fraction?
  - Can we include hydro smartly?
- Lithium flowsheets:
  - Full battery focus. Li recovery now at high levels, despite initial focus on other components
  - Discharging, disassembly, extensive comminution and sorting
  - Has evolved from open debate to mix of big players and startups with proprietary know-how
  - Collection network, scale up and more centralized industrialization may have overtaken Pb
- Two very different metals need different approach, but industries can interact and learn