 

Materials Production

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2.83/2.813

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Readings

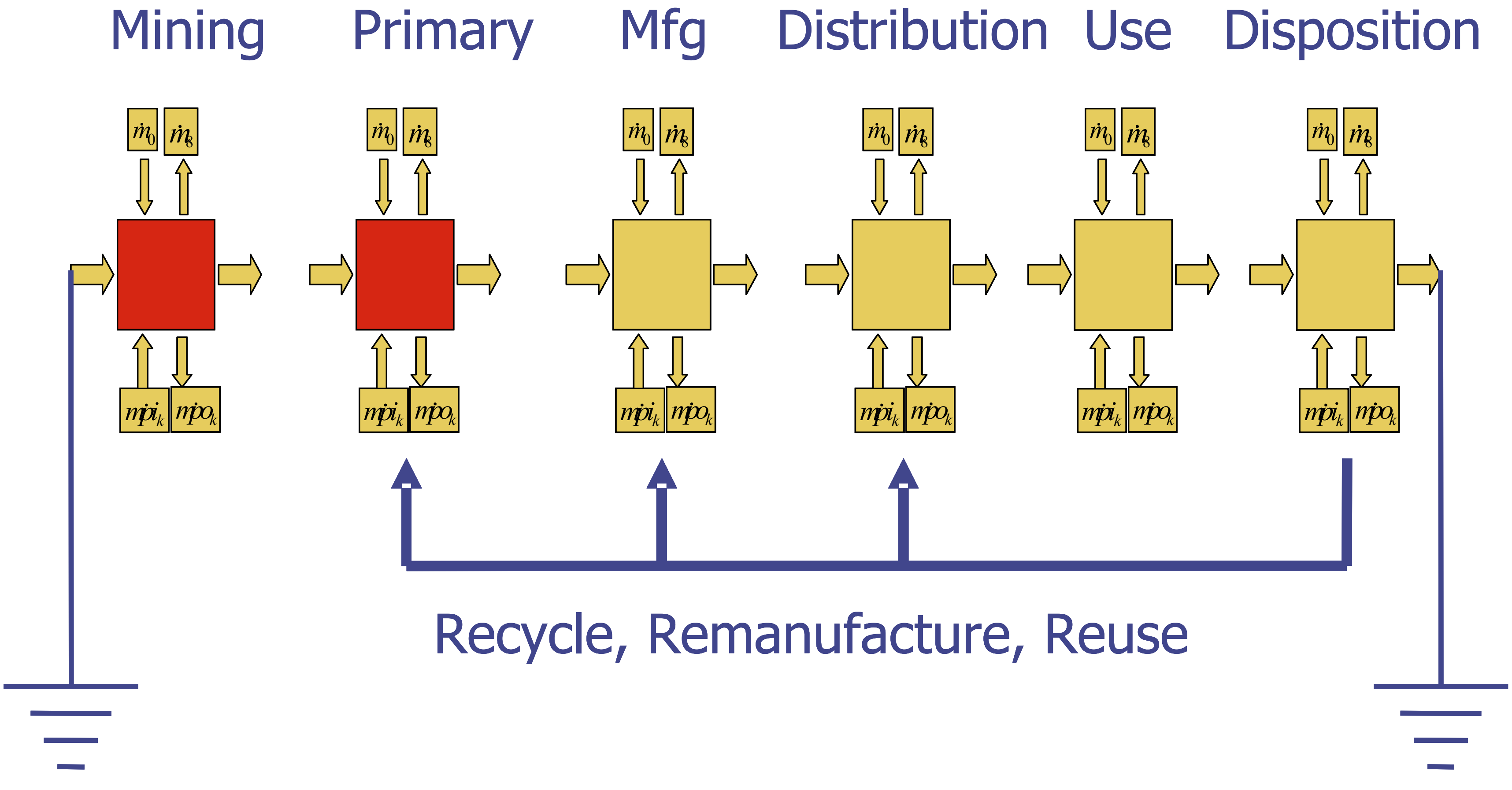
#6 3/2 Materials Production

a) Masini and Ayres, **"An Application of Exergy Accounting to Five Basic Metal Industries"**, 2001 (click here for PDF).

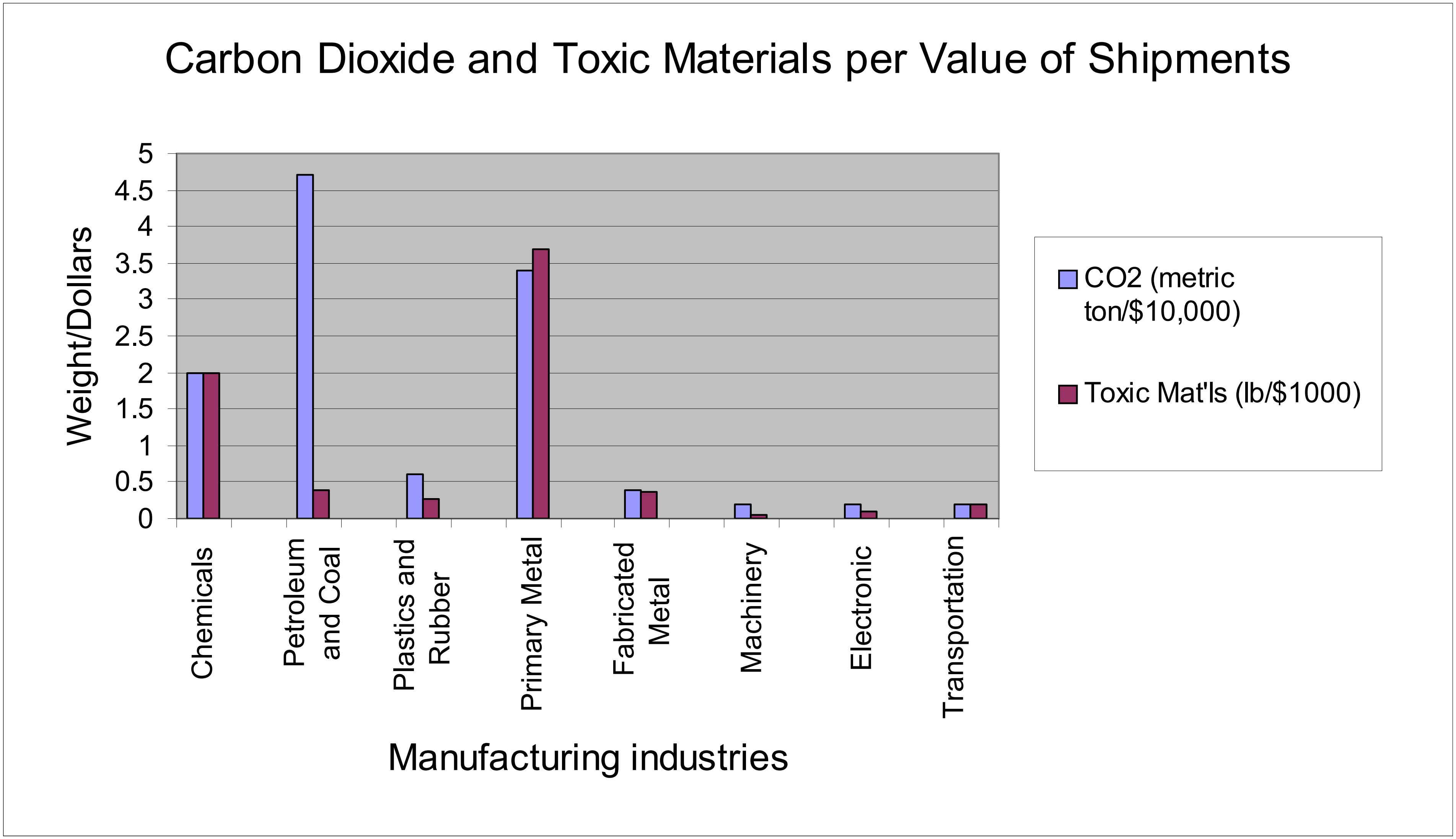
b) Lagos, **"Copper in Health and the Environmental: Evolving Issues and Market Impacts"**, Erzmetall, 2005. (handout)

c) Graedel, et al "The contemporary European copper cycle…" Ecological Economics 42 (2002) 9-26

Materials Production



Mat’l Production and Mfg



Materials Production Issues:

- Extraction
- Refining
- Materials Flows
- Energy (Exergy)
- <u>Copper</u>, Iron, Aluminum and Zinc

Copper Ore Grades in the US

60 Resources, reserves and ore grades

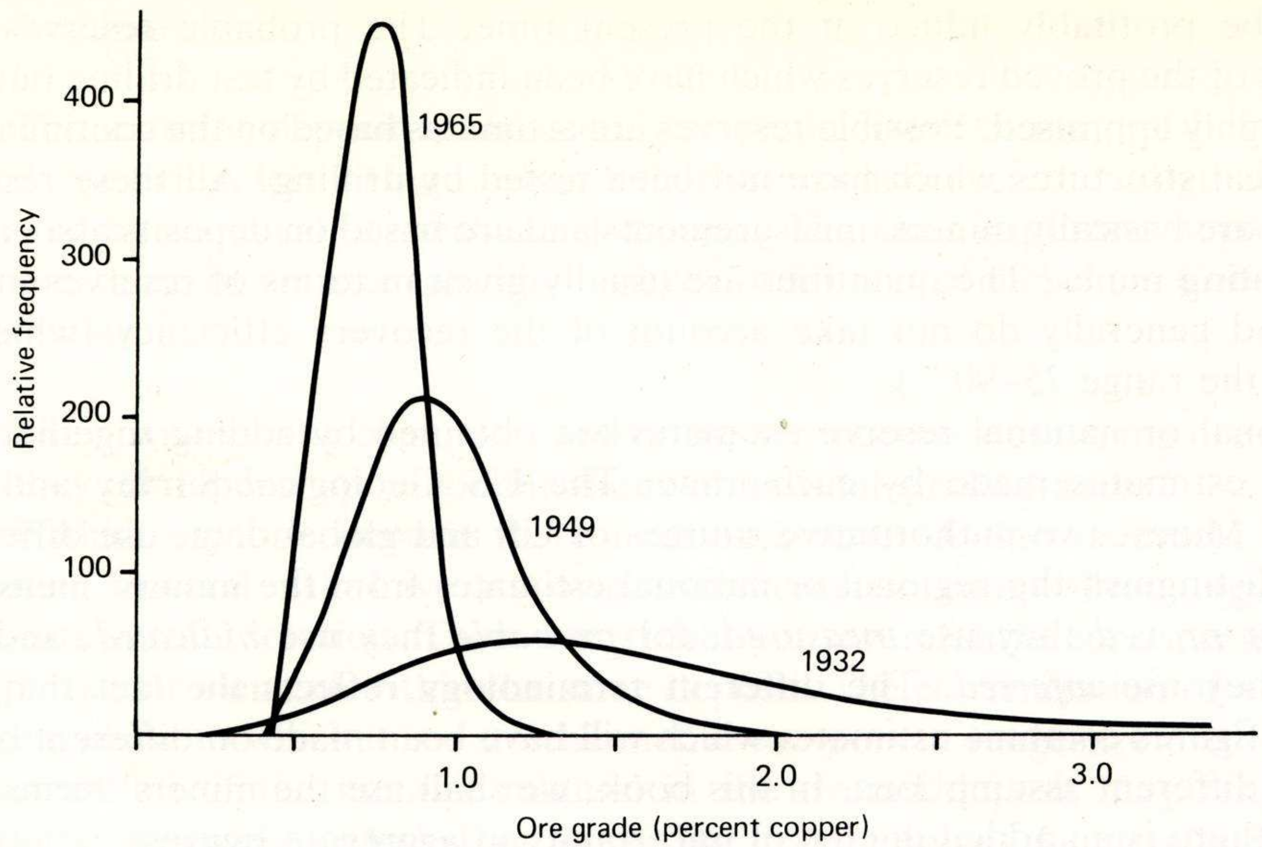
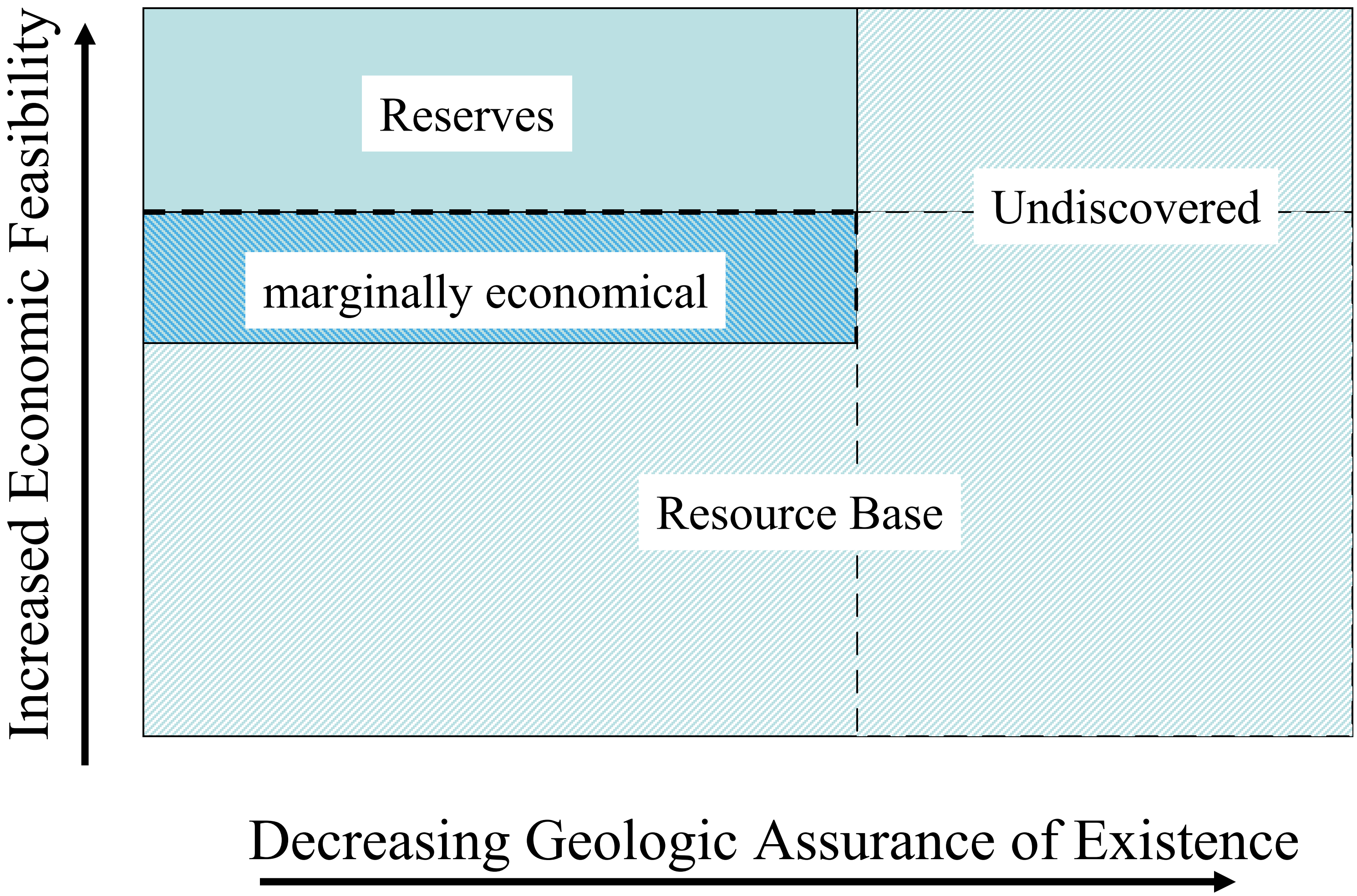


Figure 5.1 The range of copper ore grades mined in the USA for three selected years (*Source*: Phillips and Edwards[4])

McKelvey Box



Adapted from C. F. Murphy, and McKelvey, 1972

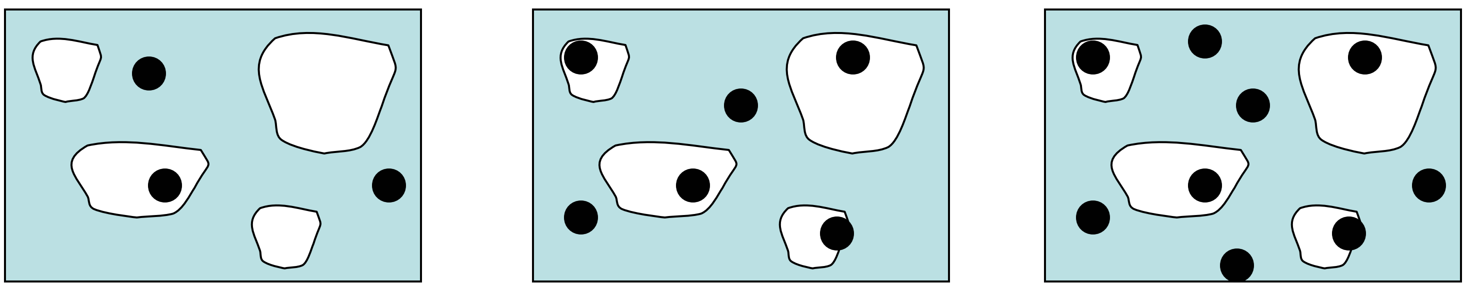
Definitions

- Reserves - the amount of a commodity that has been located and which can be economically extracted with current technology and prices
- Resources - reserves plus an estimate of the amount the commodity that is as yet undiscovered but would be profitable to extract plus an estimate of located deposits that are expected to be profitable in the near future due to emerging technologies (cost reductions) or moderate price increases
- Resource Base - all of a commodity contained in the earth's crust

C. F. Murphy

Probability of Discovery

- Function of size of target area and number of attempts to locate a field
  - Early in discovery process, low number of hits
  - Late in discovery process, low probability of undetected field



- Produces bell shaped curve

C. F. Murphy

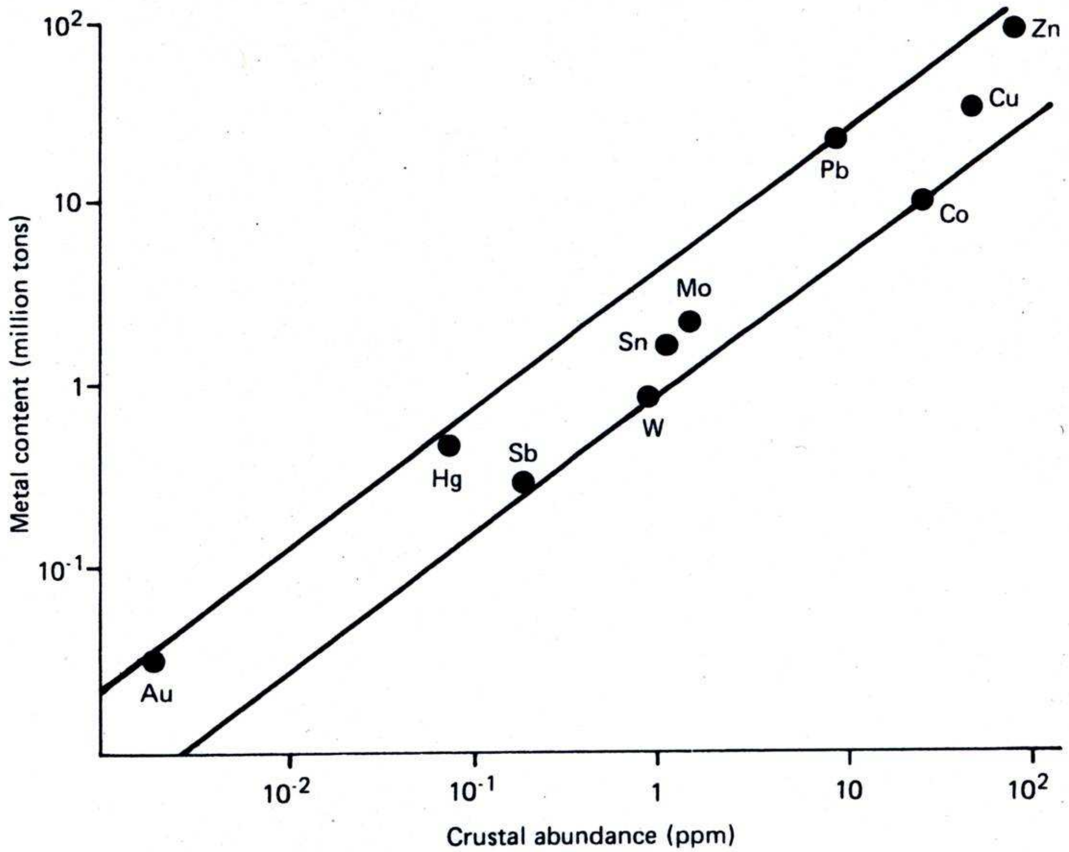


Figure 5.19 The metal contents of the largest known deposits of the geochemically scarce metals versus the crustal abundance of the elements (*Source*: Skinner[23])

Source: http://encarta.msn.com/media_461533479_761561391_-1_1/Open-Pit_Copper_Mine_Utah.html

Chuquicamata, Chile

drilling rig in underground mine in the Głogow area of Poland

Copper concentrations in this area are about 2%

energy requirements for mining and milling, possible future trends

underground ~ 1000/g (MJ/t metal)

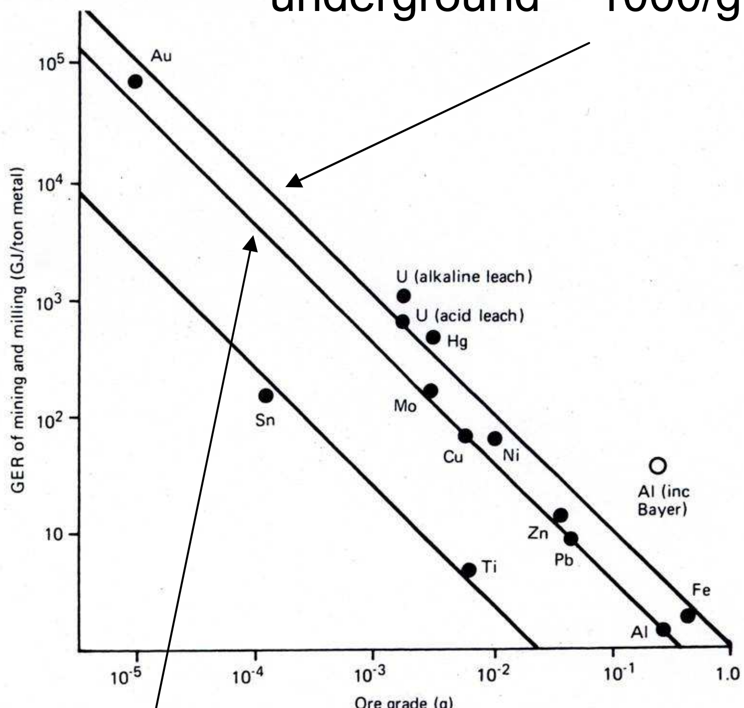


Figure 7.9 The variation of the ger of mining and milling (F_{mm}) with ore grade (g)

open pit ~ 400/g (MJ/t metal)

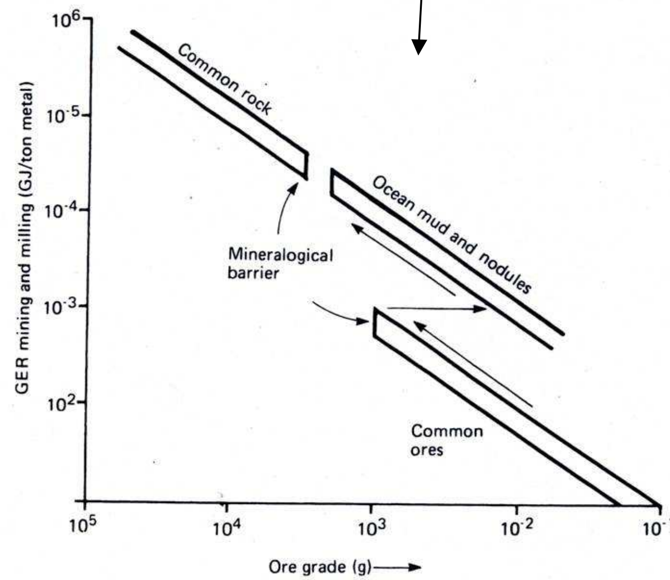


Figure 7.11 A possible sequence of sources of copper and their energy requirements (*Source*: Skinner[30])

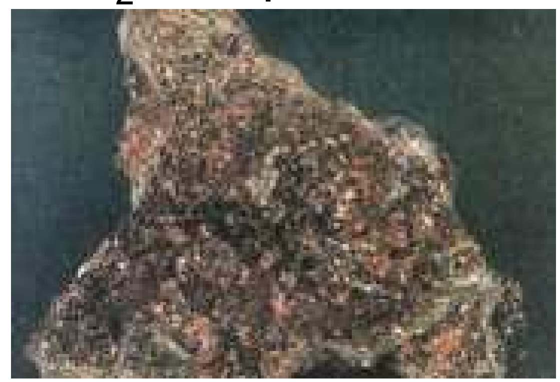
Chapman and Roberts p 113 & 116

Main Ore Types for Copper

globally 90% sulfides, 10% oxides

Cu_2S: Chalcocite

$Cu_2$0: Cuprite



$CuFeS_2$: Chalcopyrite (50% of Copper Production)

$Cu_2CO_3(OH)_2$: Malachite

Sources: http://en.wikipedia.org/

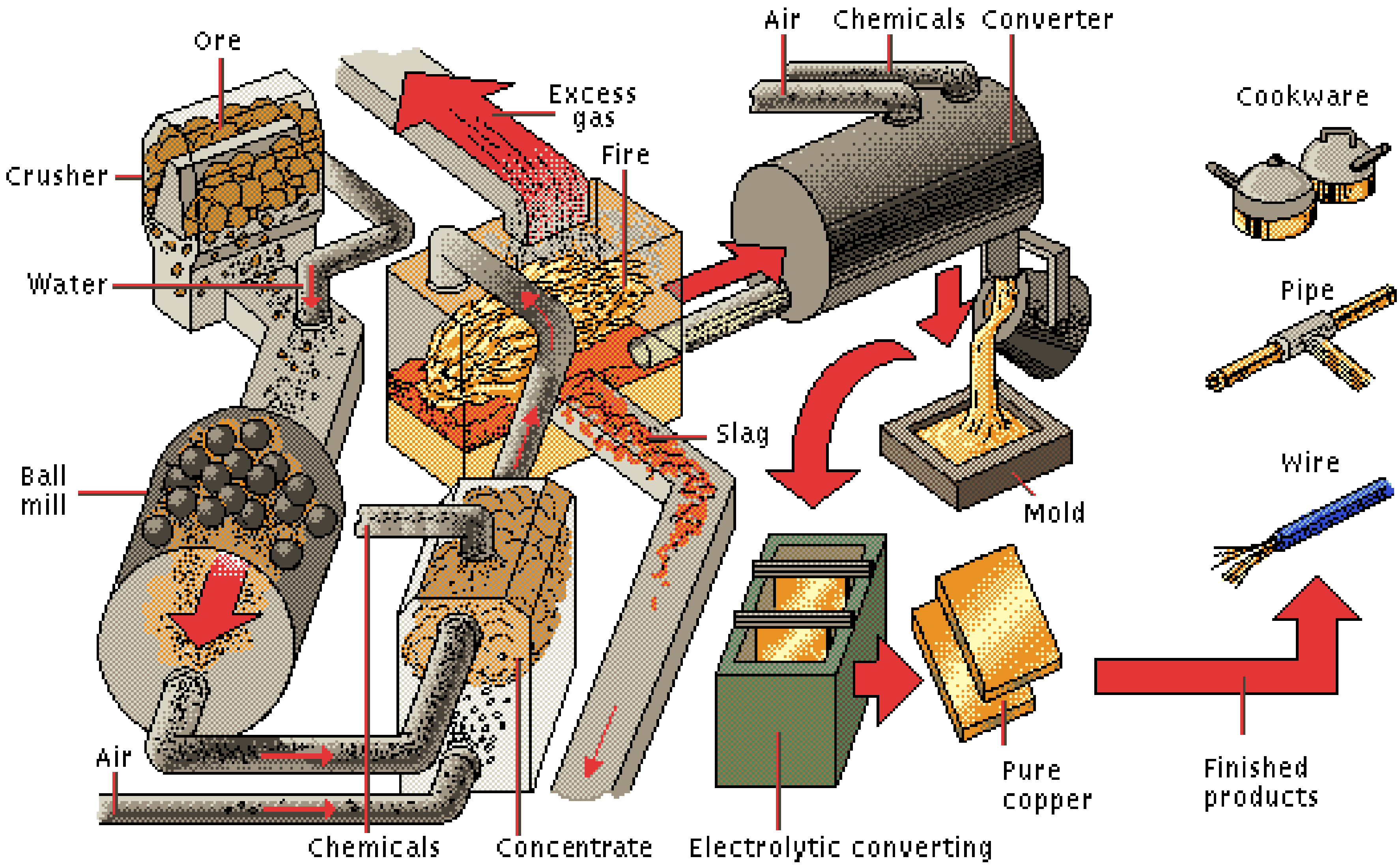
Acid mine drainage

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4$$

Głogow* Copper Smelter

*pronounced Gwogov

Copper Smelting Process

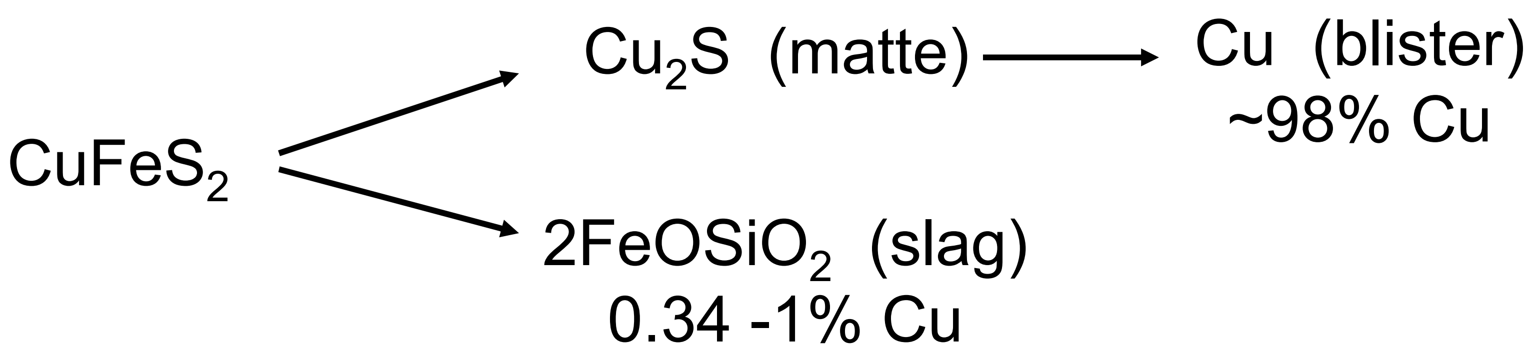


Source: http://encarta.msn.com/media_461533478_761561391_-1_1/Production_of_Copper.html

Copper Smelting Process

1) Copper Ore (~ 1%) → Concentrate (~20 to 35%)
   - milling, flotation, separation

2) Roasting and Smelting



Copper Smelting Process

3) Roasting and Smelting

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$

$xFeO + ySiO_2 \rightarrow (FeO)_x \cdot (Si0_2)_y$ - slag

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$ (blister copper ~98%)

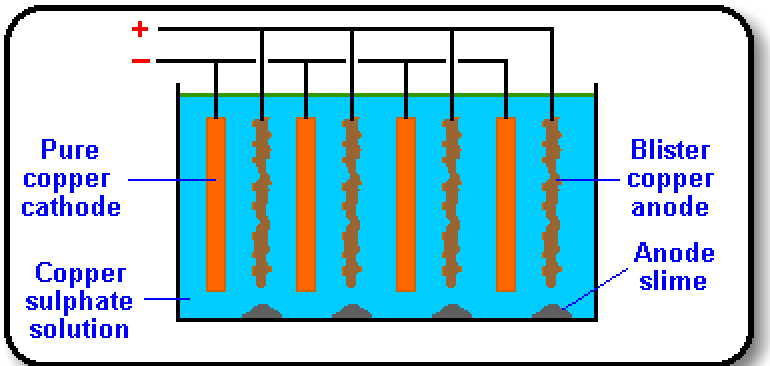
4) Electrolytic Refining (99.99%)

sulfuric acid electrolyte

anode mud (1:100) contains (Cu, Ag, As, Se, Bi, ..Au, Te…)

Source: http://encarta.msn.com/media_461547490_761561391_-1_1/Smelting_Copper.html

electro-refining of copper



$$Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2e^-$$

Cu	Ag	Au	Se	Te	As	Sb	Bi	Fe	Ni
20	5	0.5	5	1	5	1	3	0.25	0.05

Anode slime analysis (%) see Greadel et al (2002)

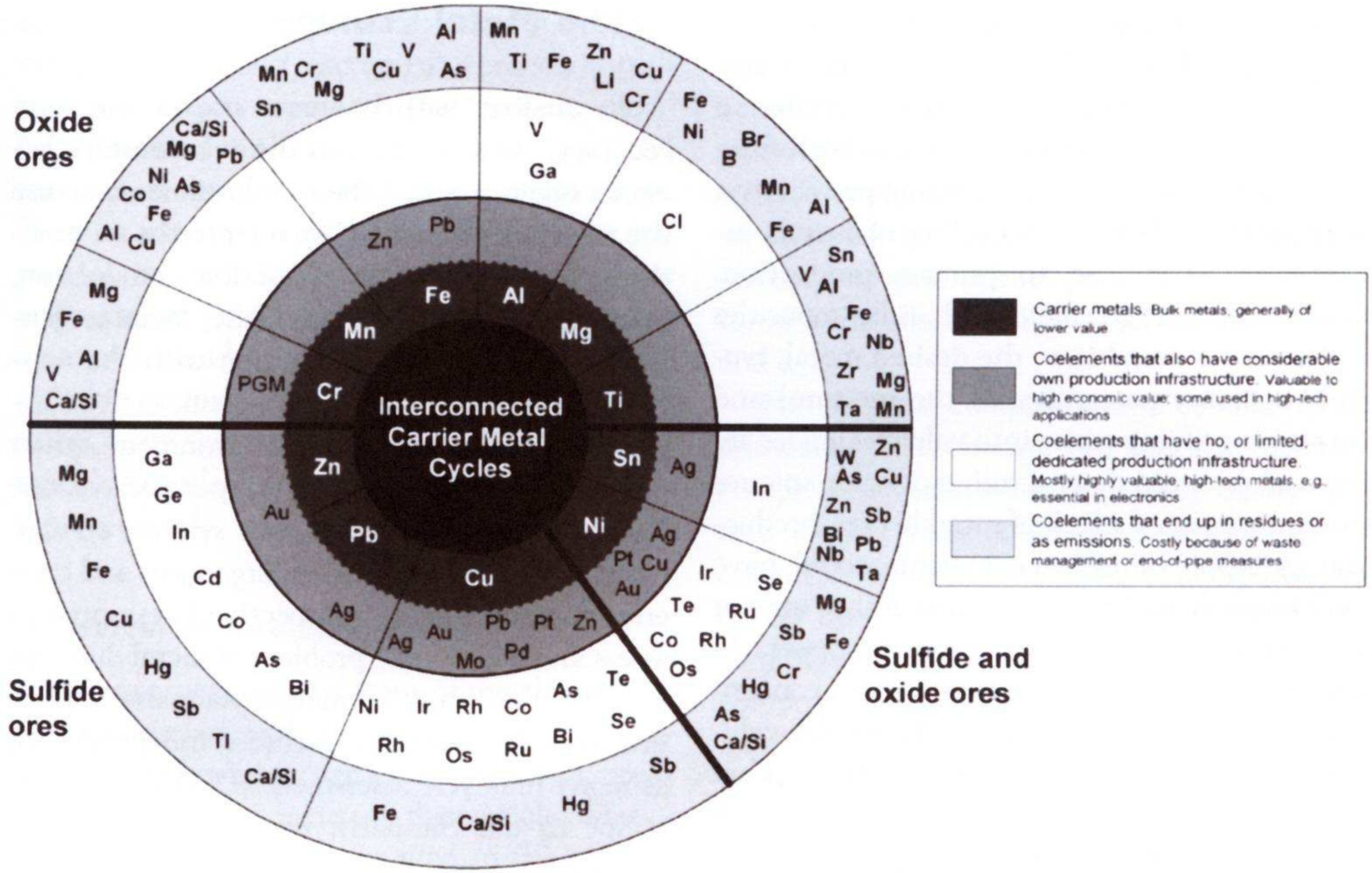
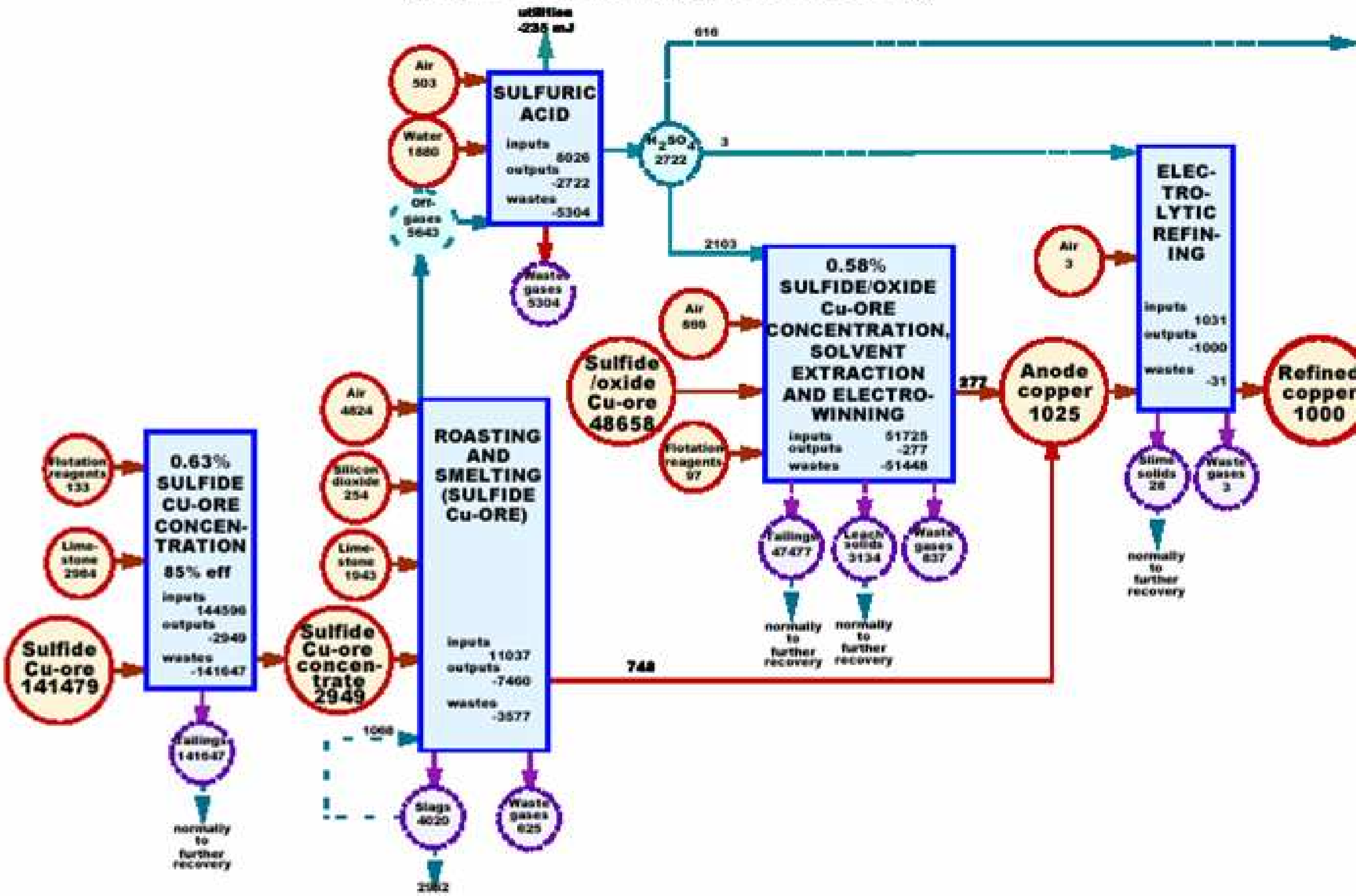


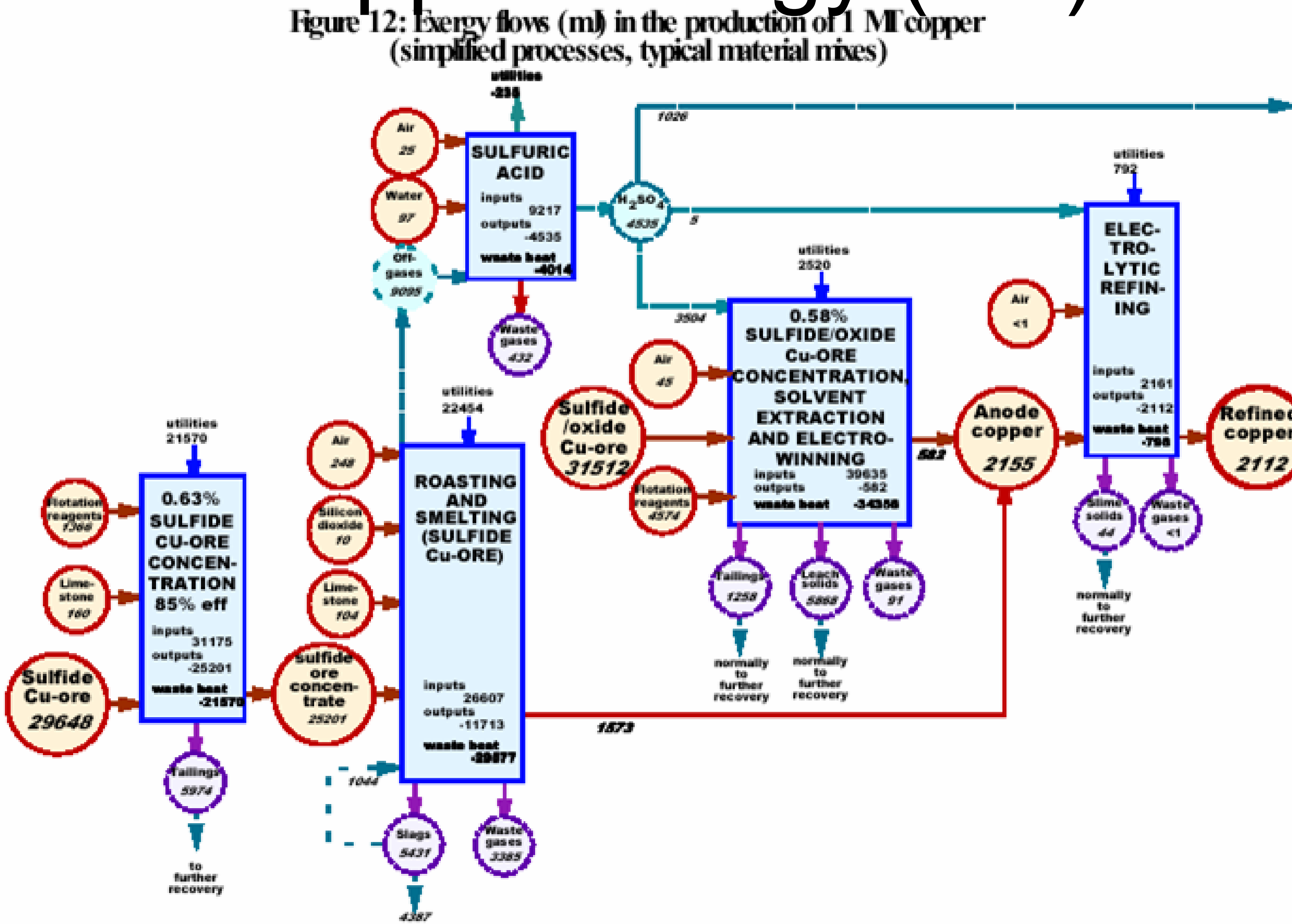
Figure 1 The metal wheel showing metal linkages in natural resource processing, illustrating the capacity of available metallurgical processes to deal with impurities in their (primary or secondary) feed. The sectors or wedges of the circle represent the metallurgy of the carrier metal. The bold radial lines divide metallurgical recovery into three main areas, namely sulfide metallurgy, oxide metallurgy, and a mixture of sulfide and oxide metallurgy, whereas the lighter radial lines separate the metallurgy of individual commodity metals. Coelements are economically and technologically valuable minor elements or impurities found in ores of carrier or commodity metals (Verhoef et al. 2003).

Copper Mass Flows (US)

Figure 5: Mass flows (kg) in the production of 1 MT copper
(simplified processes, typical material mixes)

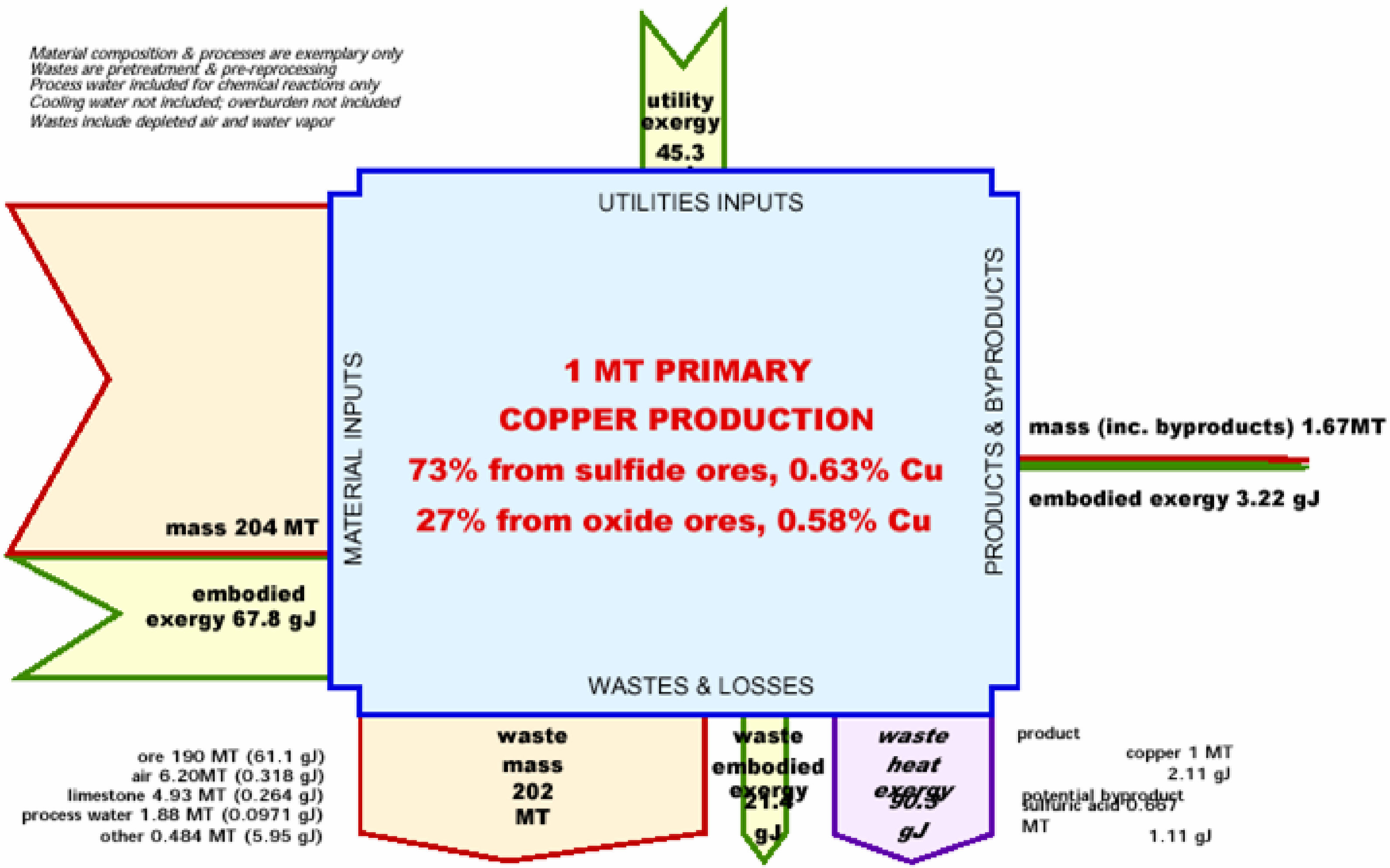


Copper Exergy (US)



Copper Summary (US)

Figure 13: Primary copper mass and exergy flows



Tailings pond at Głogow, Poland

.02X.9 to smelt, .02X.1 to tailings
these tailings will be mined in the future

Summary from Masini & Ayres Exergy Analysis for U.S. Industries

Metal	B^o(MJ/kg)	B_{lost}(MJ/kg)	B^o / B_{lost}	**Ore grade (percent)**
Steel	6.7(Fe)	23.6	28.5%	Ore 53% + scrap 93%
Aluminum	32.9	303.4	10.9%	26% Alu (bauxite)
Copper	2.1	179.1	1.2%	0.6%
Zinc	5.2	225.8	2.3%	9%

the fuel requirements of smelting

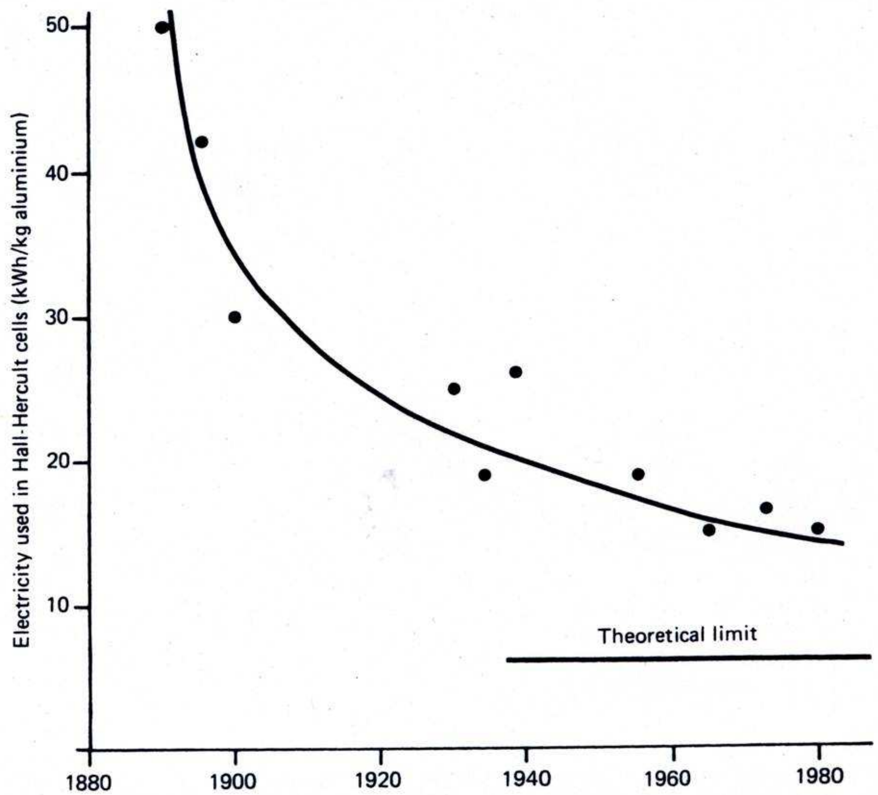


Figure 6.7 The trend in the use of electricity in aluminium production

* Recently coke consumption has been reduced further than indicated on the figure by the use of oil injection in blast furnaces. This use of oil provides an alternative source of carbon, a source which does not also have to fulfil the structural role performed by coke.

possible future trends in energy use trends reflect lower ore grades

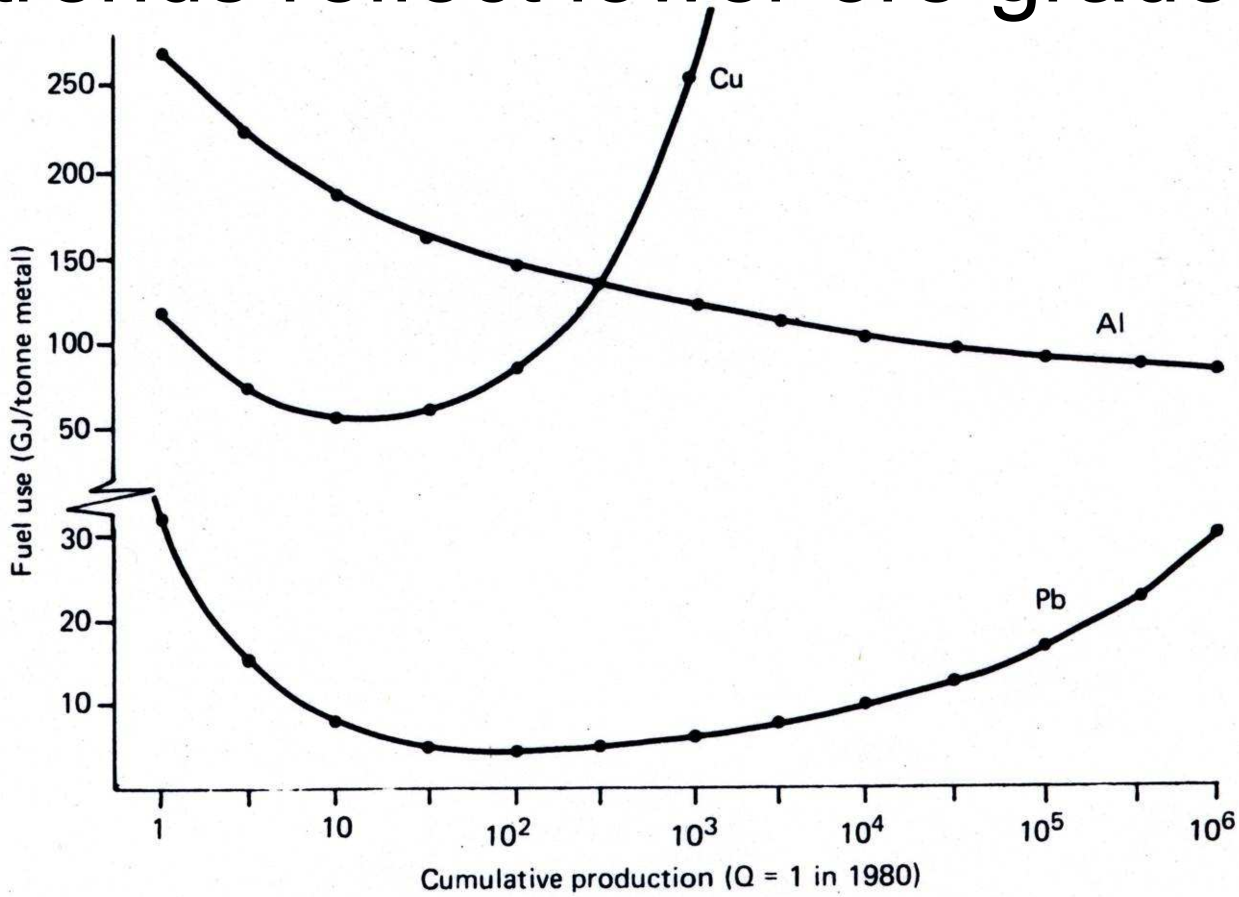


Figure 9.6 The trends in fuel use as a function of cumulative production for several metals (note change in vertical scale)

bio-toxicity of copper

- Copper in drinking water (USEPA, WHO)
- Copper in fresh water (5 pbb)
- bioavailability and the biotic ligand model "BLM"
- gastrointestinal effects (NOAEL 2mg/L)
- Wilson's disease and 5% of population
- aggressive water

Check out these websites for copper mining and smelting

http://www.na-ag.com/NA_en

http://www.mining-technology.com/projects/kghm/

Iron: Important oxide ores

Hematite: Fe_2O_3

Magnetite: Fe_3O_4

Taconite

Sources: http://en.wikipedia.org/ &
http://resourcescommittee.house.gov/subcommittees/emr/usgsweb/materials/images/imgTaconite.jpg

Taco – night
(not to be confused with Taconite)

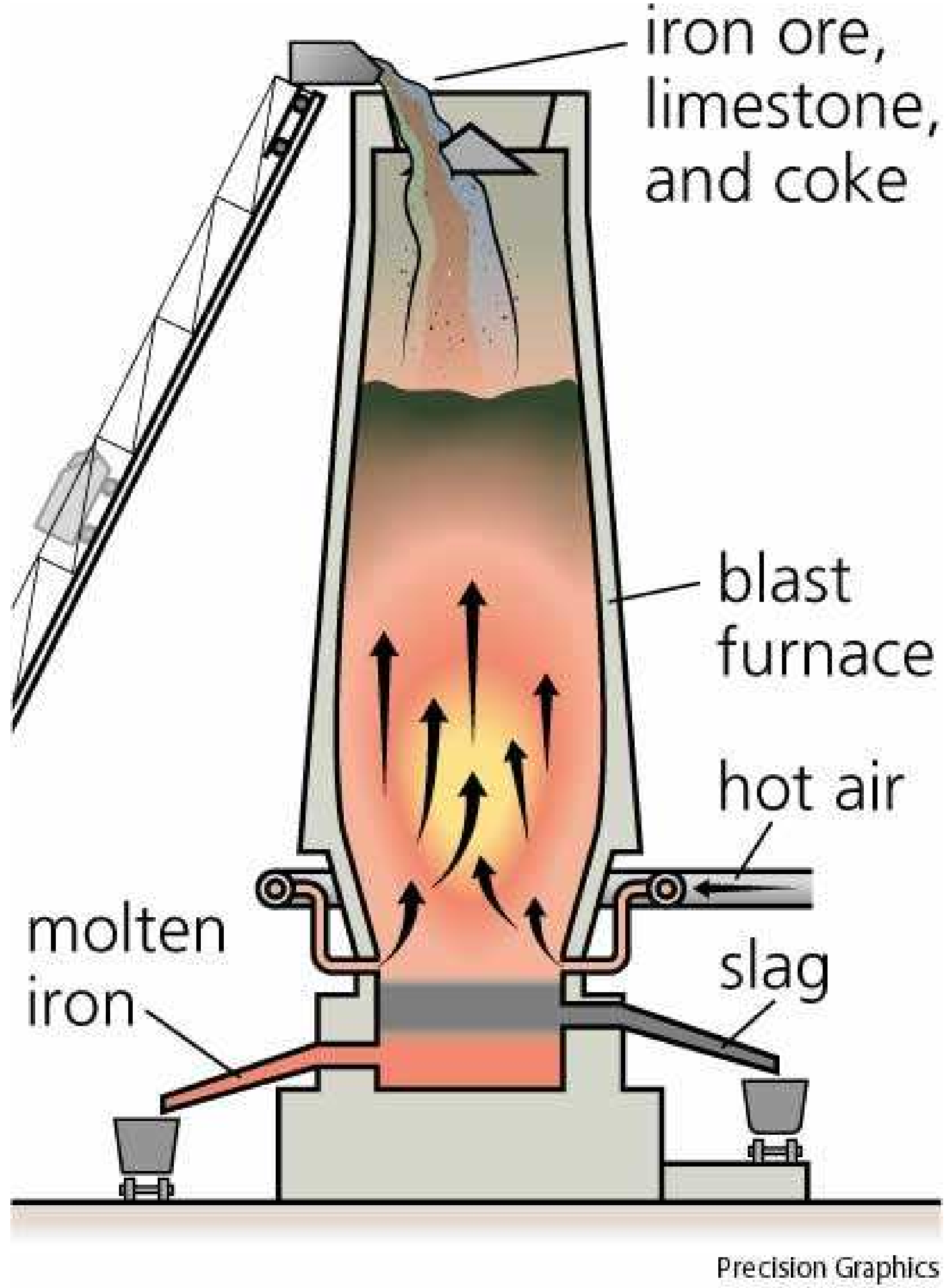
This slide brought to you by Tacoo Bell

TACO BELL

Iron Blast Furnace

<u>Materials required:</u>

1. Iron Ore
2. Carbon (coke is used both as fuel and reducing agent).
3. Hot air (hot enough to ensure combustion of the fuel).
4. Flux (removes earthy matter – turns into slag)
5. Slag (combination of calcium carbonate, silica, alumina and other impurities).



Source: http://www.yourdictionary.com/images/ahd/jpg/A4blfurn.jpg

Reactions taking place in the furnace:

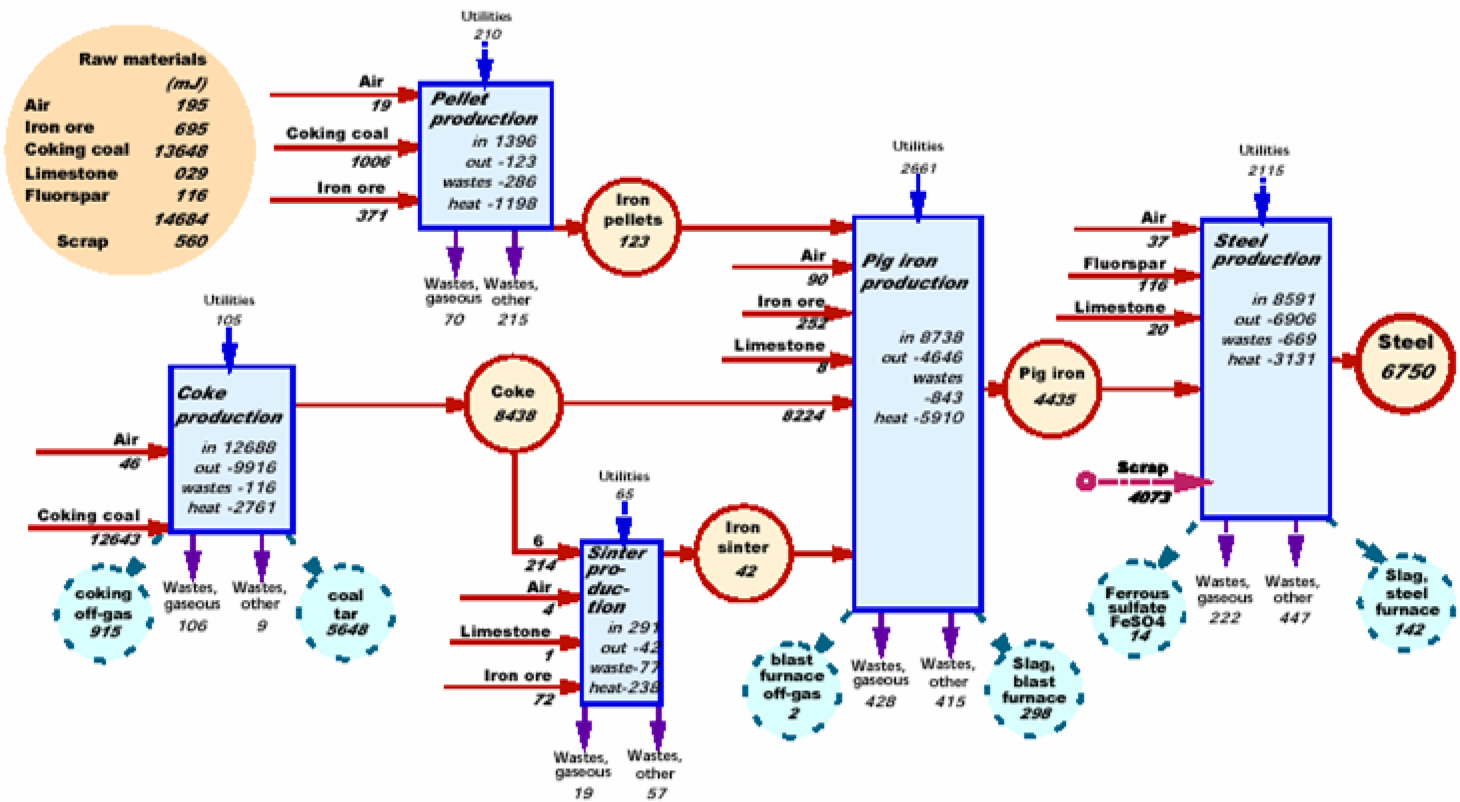
- $2\ C + O_2 \rightarrow 2\ CO$ (1300 °C)
- $CaO + SiO_2 \rightarrow CaSiO_3$ (1200 °C)
- $FeO + CO \rightarrow Fe + CO_2$ (800 °C - 1000 °C)
- $CaCO_3 \rightarrow CaO + CO_2$ (800 °C - 1000 °C)
- $CO_2 + C \rightarrow 2\ CO$ (800 °C)
- $Fe_3O_4 + CO \rightarrow 3\ FeO + CO_2$ (600 °C)
- $3\ Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2$ (450 °C)

Blast Furnace

Source: http://www.ssabox.com/news/Imagebank/blast%20furnace4.jpg

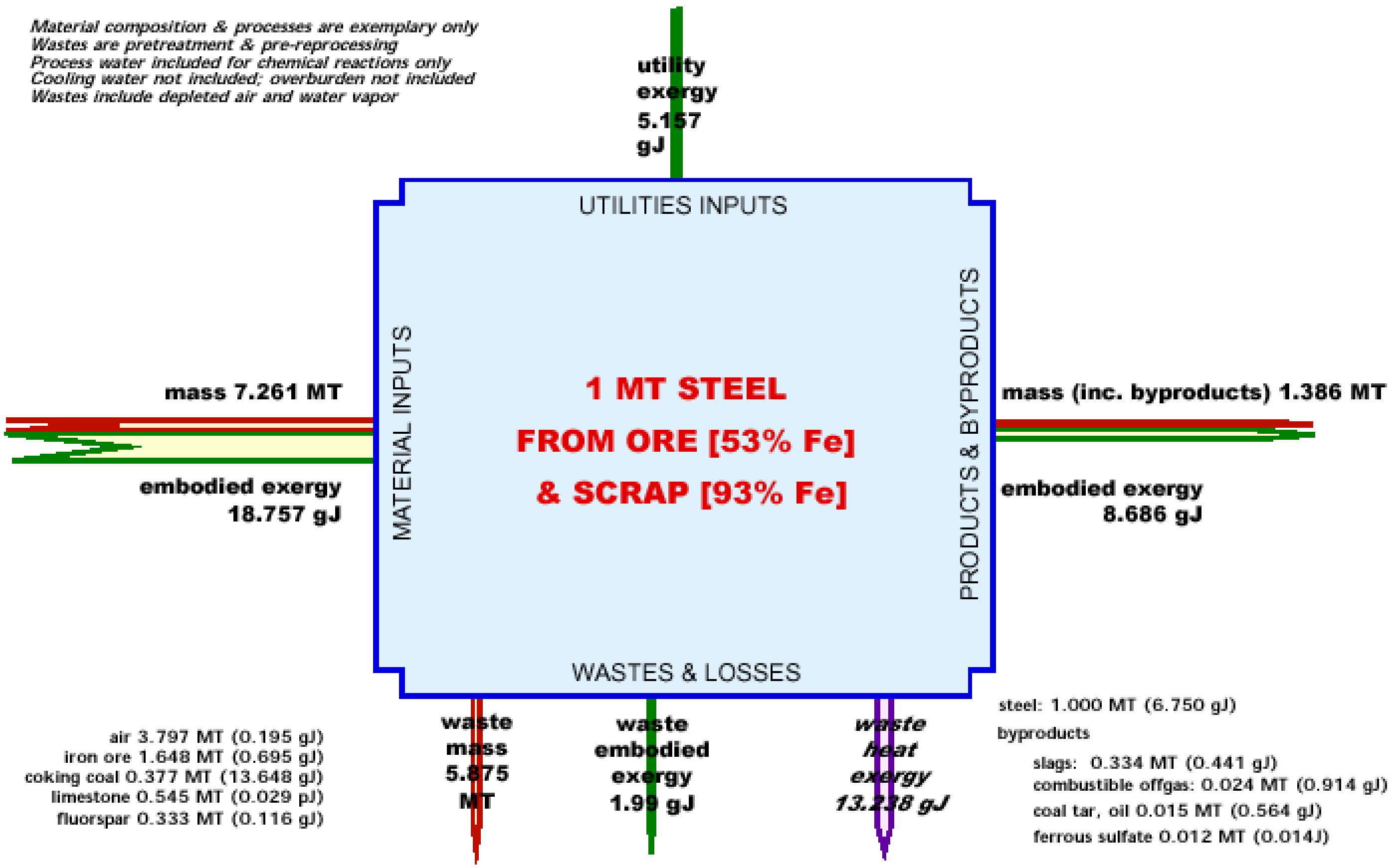
Steel Exergy (US)

Figure 8: Exergy flows (mJ) in the production of 1 MT steel (simplified processes, typical material mixes)



Steel Summary (US)

Figure 9: Steel unit mass and exergy flows



Aluminum

It is the most abundant metal (7% of the earth's crust) but one of the most difficult metals to refine

Aluminum occurance:

Bauxite : $Al_2O_3{\cdot}2H_20$

Cryolite: Na_3AlF_6

+ many silicates such as clay: $H_2Al_2(SiO_4)_2{\cdot}H_20$

Sources: http://en.wikipedia.org/ & http://www.musee.ensmp.fr/mineral//1021x.jpg

Aluminum Production:

1. *Bayer Process*: obtain Alumina (Al_2O_3) from Bauxite.

A. <u>Extraction:</u> dissolve oxides with hot solution of NaOH.

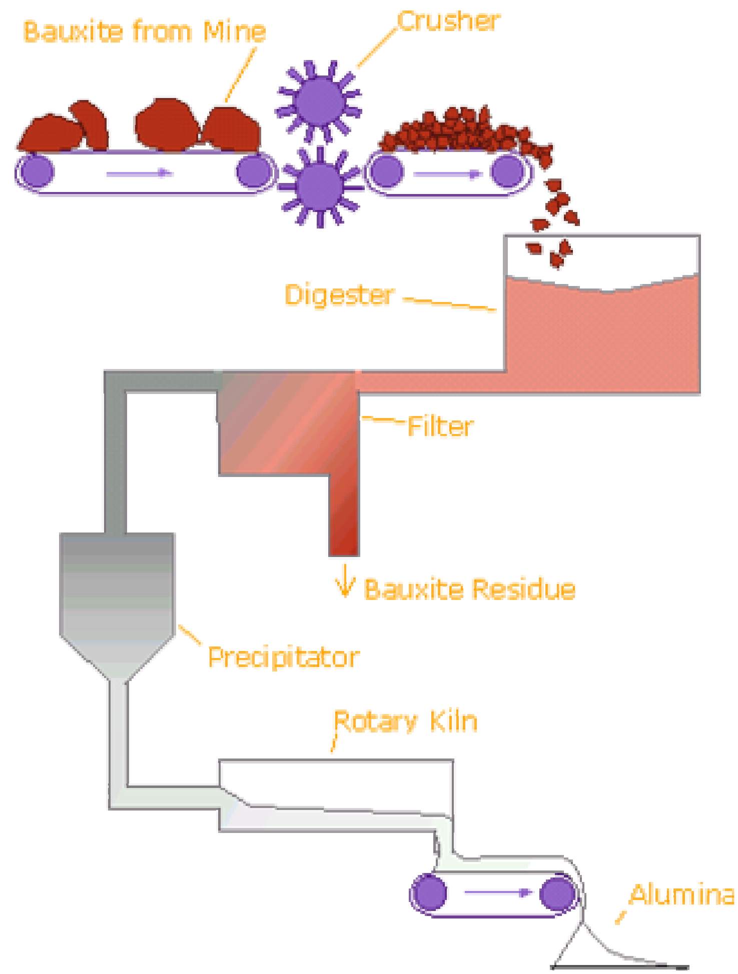
$$Al(OH)_3 + Na^+ + OH^- \rightarrow Al(OH)_4^- + Na^+$$

B. <u>Precipitation:</u> reverse of above, but controlling crystal formation.

$$Al(OH)_4^- + Na^+ \rightarrow Al(OH)_3 + Na^+ + OH^-$$

C. <u>Calcination:</u> water is driven off $Al(OH)_3$ to form alumina (aluminum oxide).

$$Al(OH)_3 \text{ ---> } Al_2O_3 + 3\ H_2O$$



Source: http://www.world-aluminium.org

2. Hall-Heroult Process
(Electrolytic Reaction).

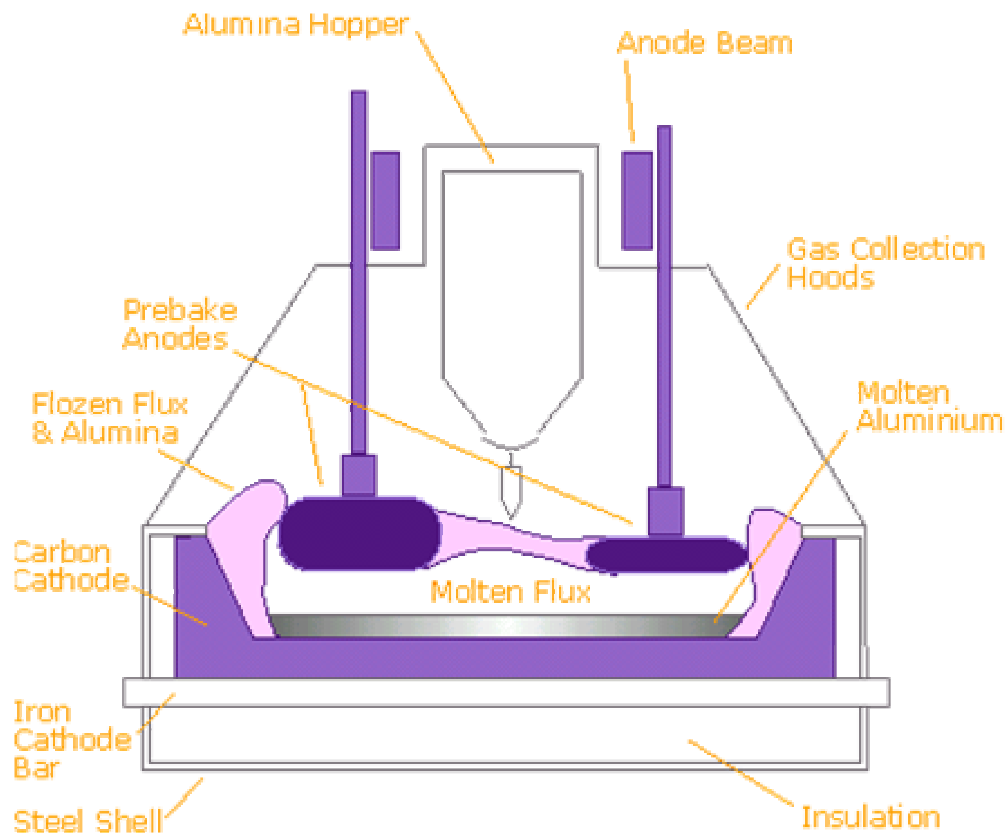
A. Al_2O_3 is dissolved in molten cryolite (Na_3AlF_6)

B. As the current passes through this mixture, (4-5 volts, 50,000-280,000 amperes) aluminum ions reduce to molten aluminum at the cathode, and oxygen is produce at the anode reacting with carbon to produce CO_2.

$$2\ Al_2O_3 + 3\ C \rightarrow 4\ Al + 3\ CO_2$$

Prebake

Anode

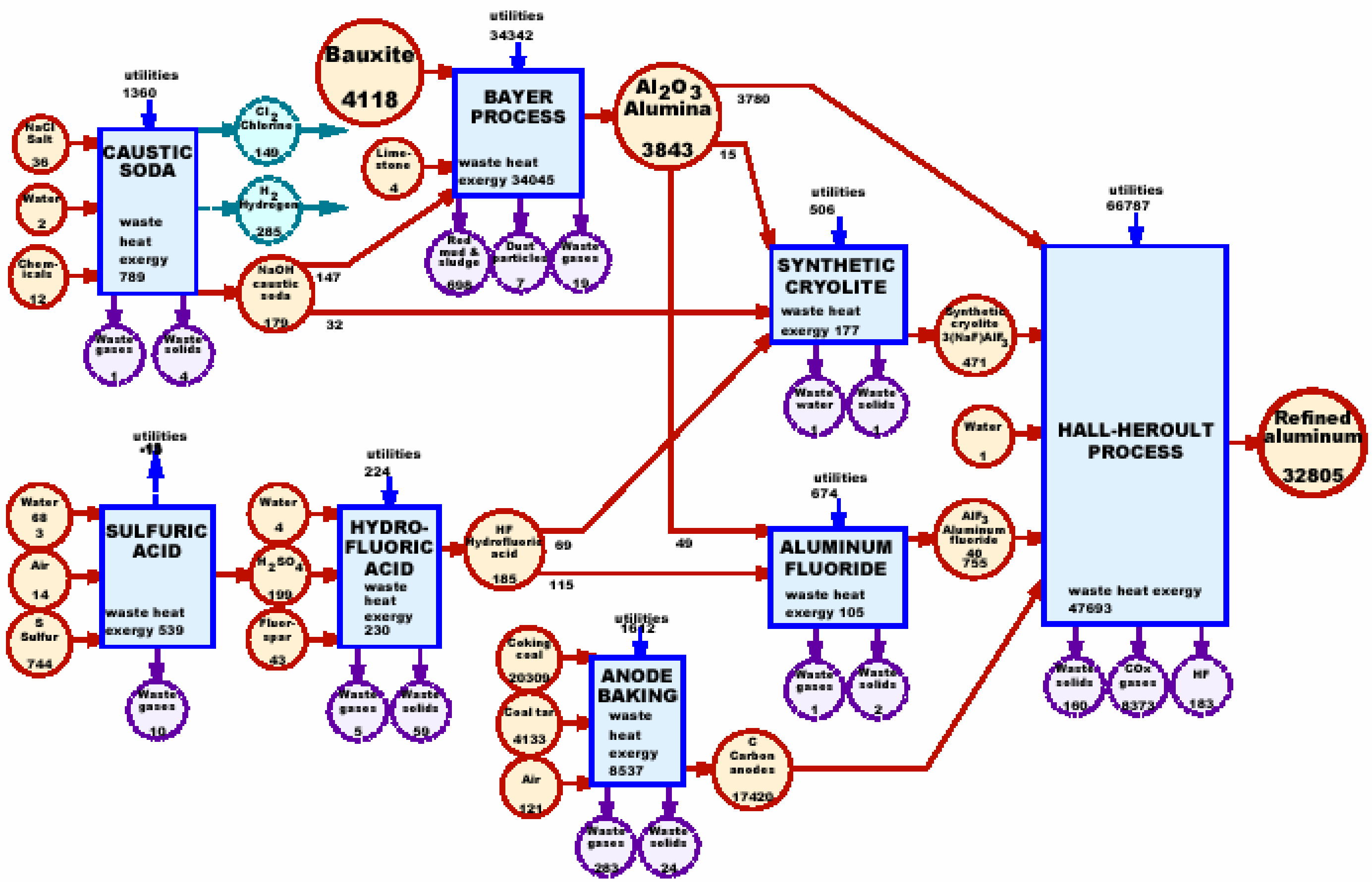


Prebake Cell

Source: http://www.world-aluminium.org

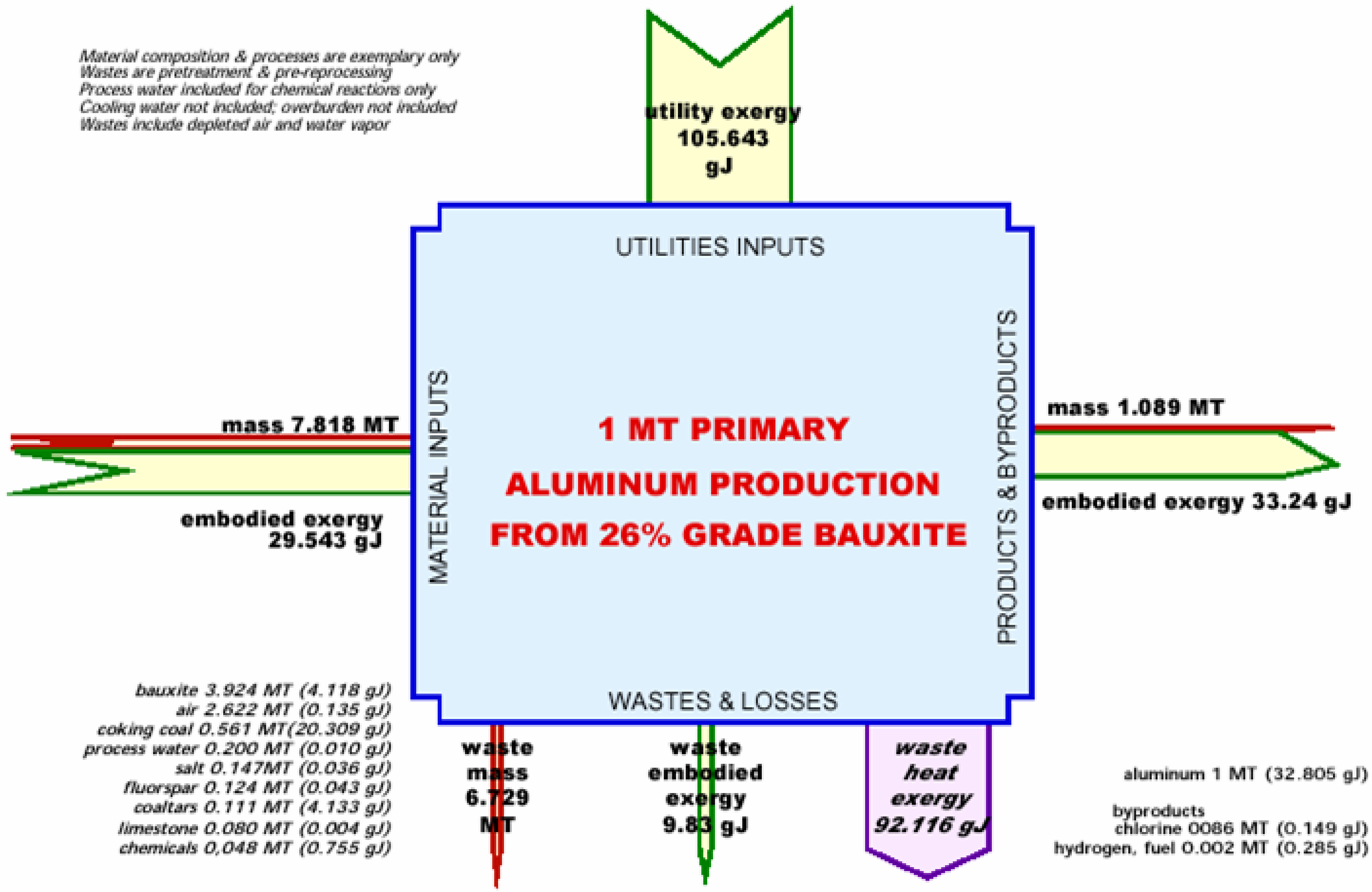
Aluminum Exergy (US)

Figure 10: Exergy flows (mJ) in the production of 1 MT aluminum
(simplified processes, typical material mixes)



Aluminum Summary (US)

Figure 11: Primary aluminum unit mass and exergy flows



With all the energy consumption → recycle

Zinc

Main Ore Types:

Sphalerite: (Zn, Fe)S

Smithsonite: $ZnCO_3$

Hemimorphite:
$Zn_4Si_2O_7(OH)2 \cdot H_2O$

Franklinite: $(Fe,Mn,Zn)(Fe,Mn)_2O_4$

Sources: http://en.wikipedia.org/ & http://webmineral.com/specimens/FrankliniteSmall.jpg

Zinc Production

1. Concentrating Zinc
   - 3 -11% as by-product of other metal
   - flotation to 52 -60%

2. Roasting

Sulfide to oxide (ZnO) → reduce/distillation

Sulfide to oxide (ZnO) → leaching and electrowinning

Zinc Production

- Roasting reactions
  - $2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$
  - $ZnS + 2\ O_2 \rightarrow 2\ ZnSO_4$

  - One can either obtain a mixture of ZnO and $ZnSO_4$ (for the leaching process) or ZnO (for the distillation process).
  - The product of the above reactions is imbedded in mixtures with other impurities.

- **Leaching** & **Distillation**.

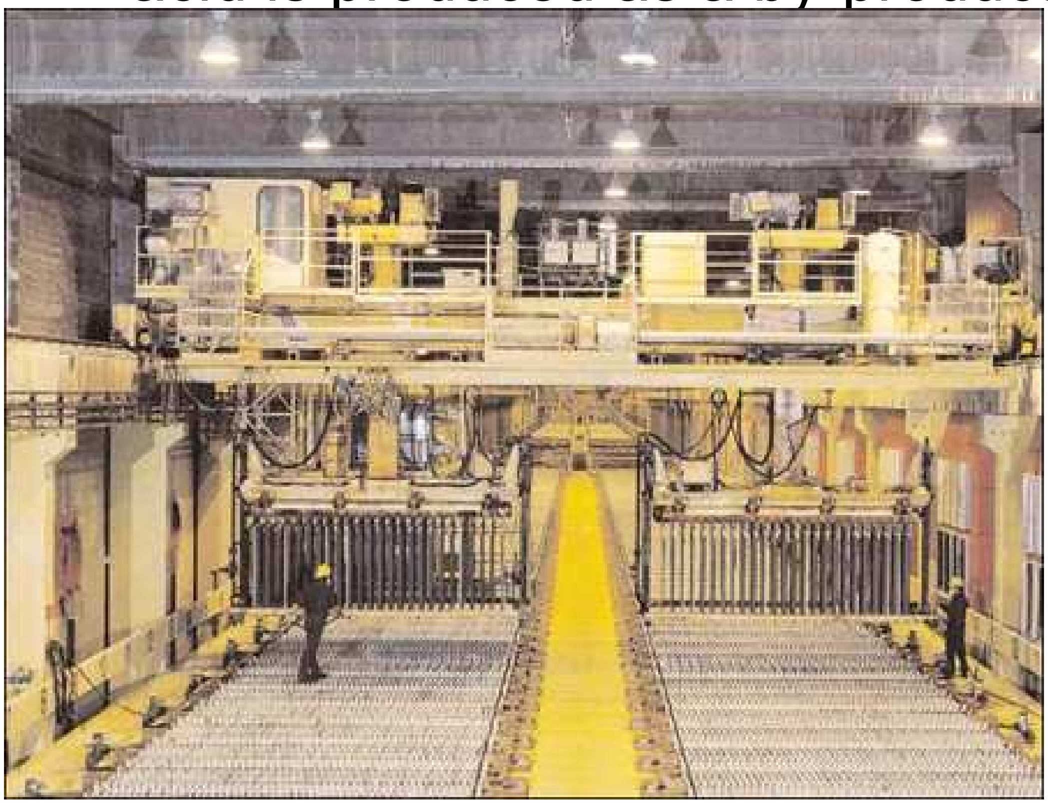
Leaching:

I. ZnO and $ZnSO_4$ are leached with dilute H_2SO_4 to produce a zinc sulfide solution .

$$ZnO+ + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

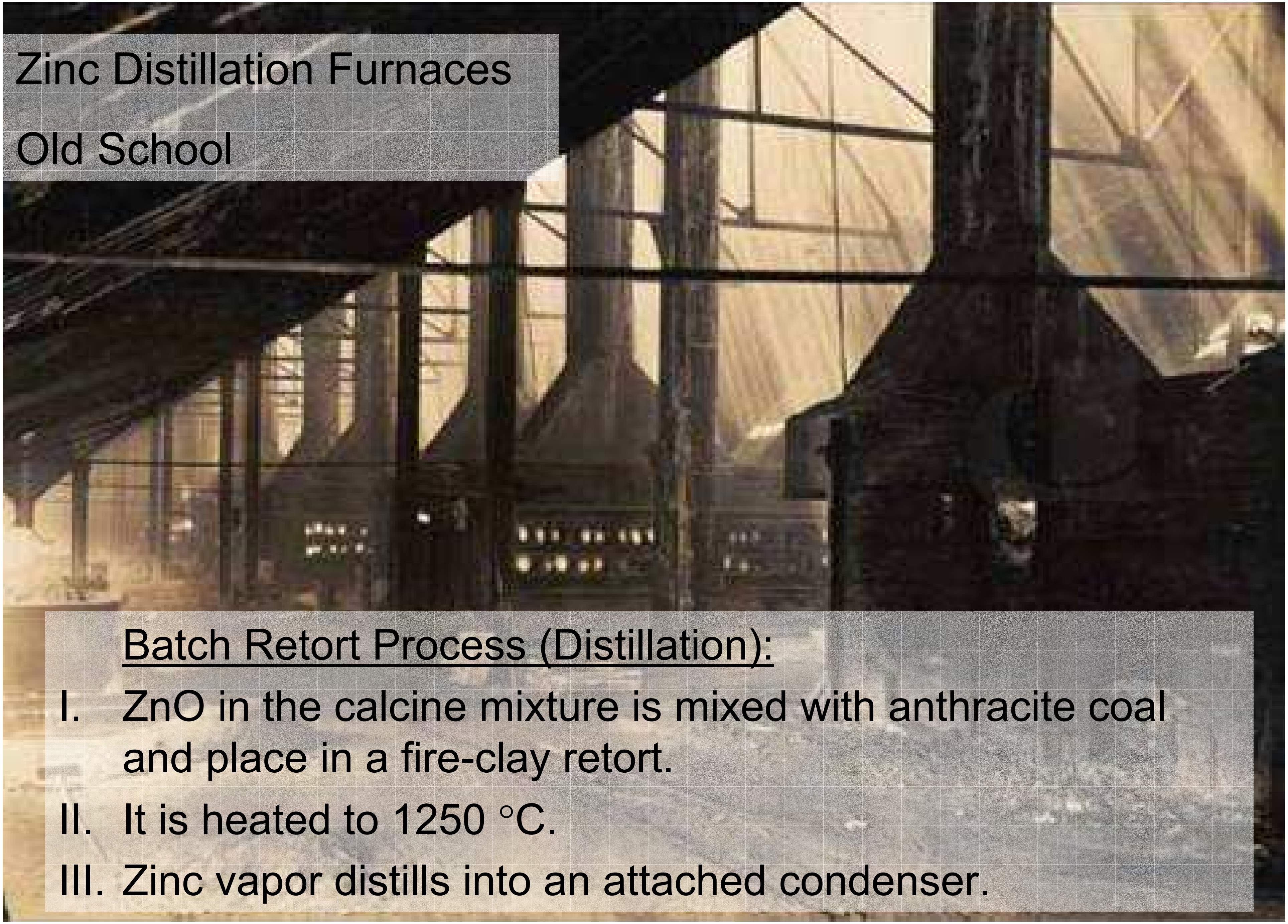
II. The solution is purified to precipitate any metal impurities.

III. An electrolytic cell is used to deposit the Zinc and sulfuric acid is produced as a by-product (can be used in step I.)



“***The Electrolytic Plant, which is the size of four football fields, consumes the same amount of power as a city of 250,000 people***”.

Source: **http://www.metsoc.org/virtualtour/processes/zinc-lead/electrolytic.asp**



Zinc Distillation Furnaces

Old School

Batch Retort Process (Distillation):

I. ZnO in the calcine mixture is mixed with anthracite coal and place in a fire-clay retort.
II. It is heated to 1250 °C.
III. Zinc vapor distills into an attached condenser.

Source: http://www.swanseaheritage.net/img/article/100000_00767.jpg

Figure 7: Mass flows (kg) in the production of 1 MT zinc
(simplified processes, typical material mixes)

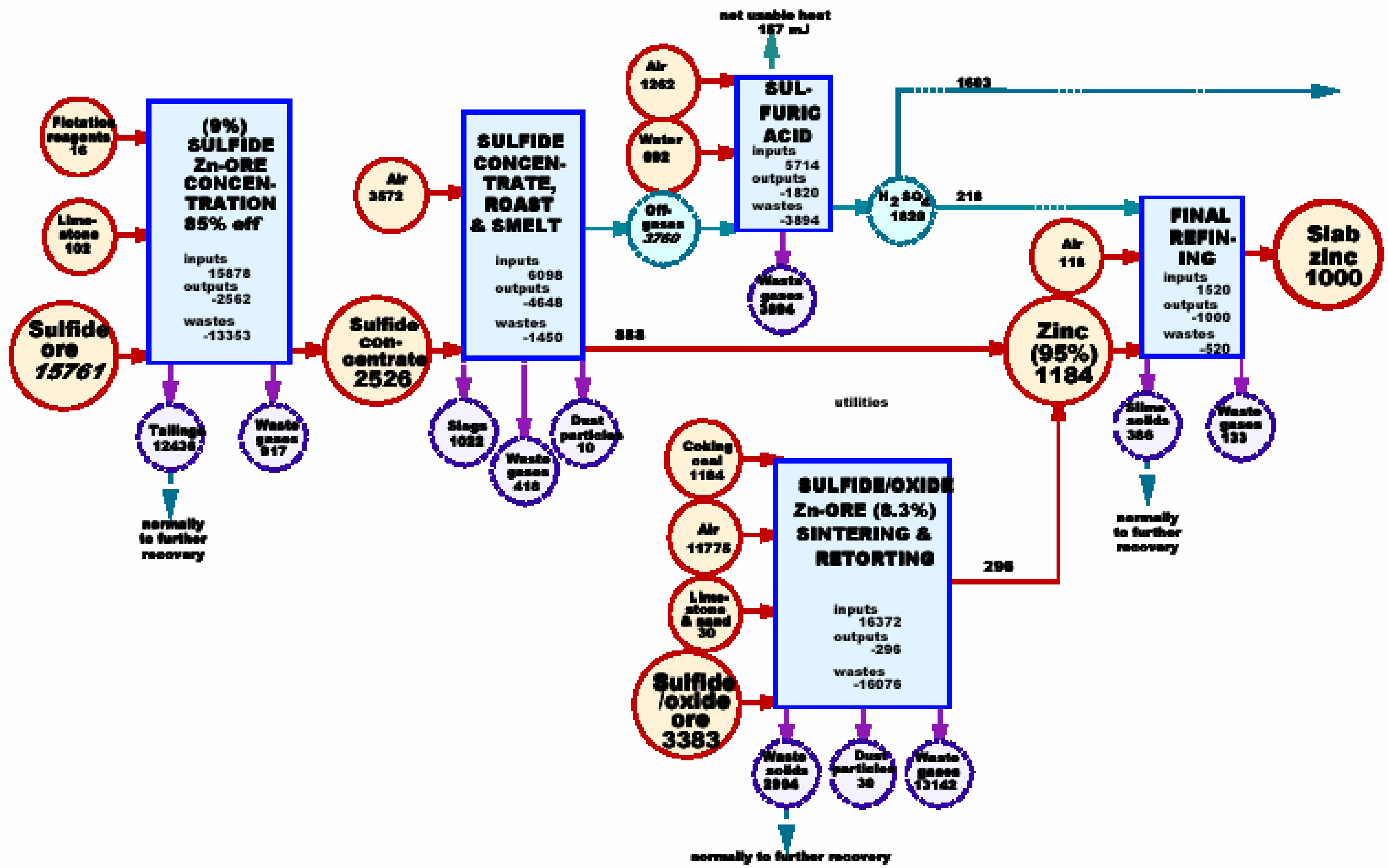


Figure 16: Exergy flows (MJ) in the production of 1 MT zinc
(simplified processes, typical material mixes)

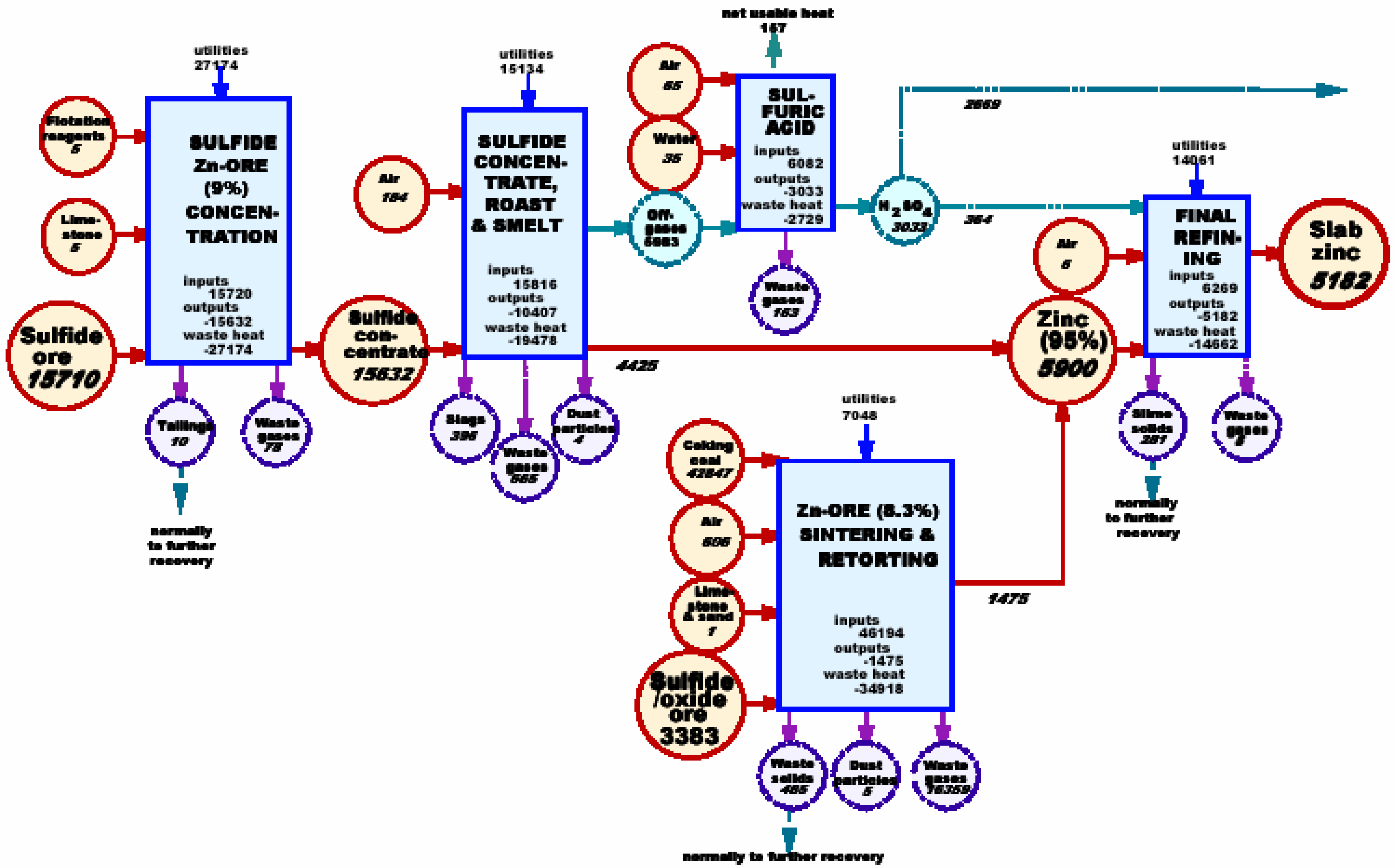
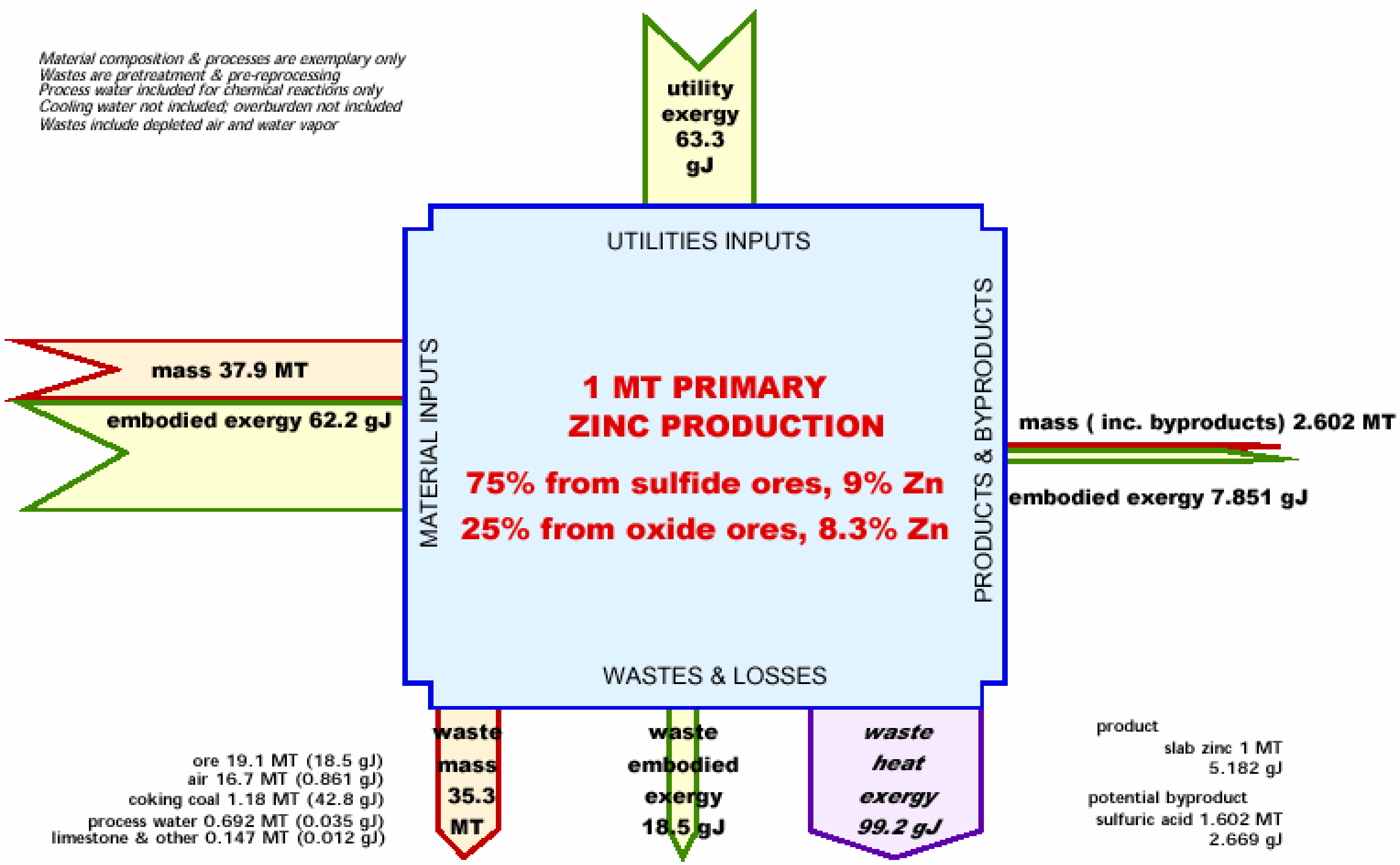
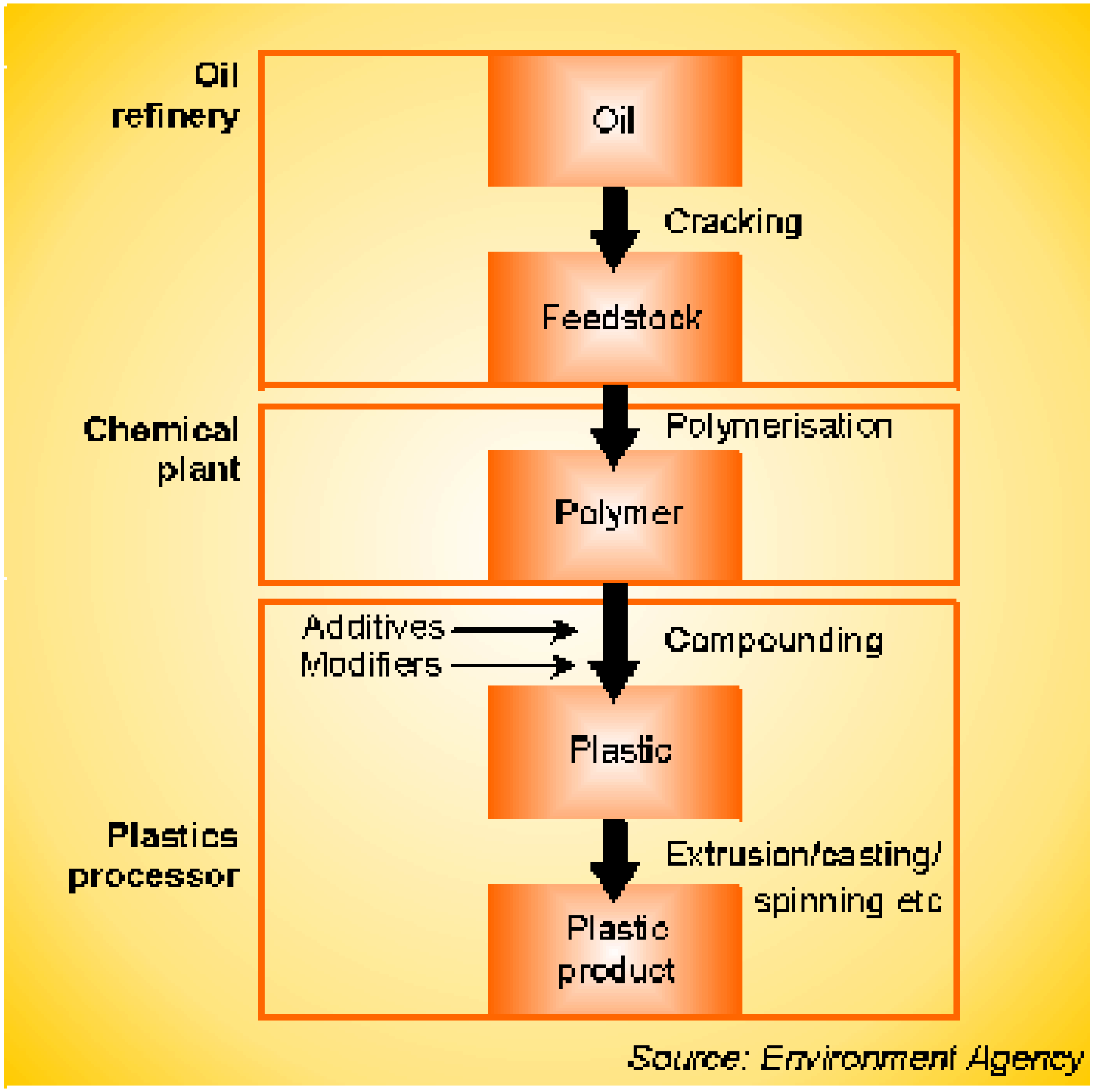


Figure 17: Overall unit zinc mass and exergy flows

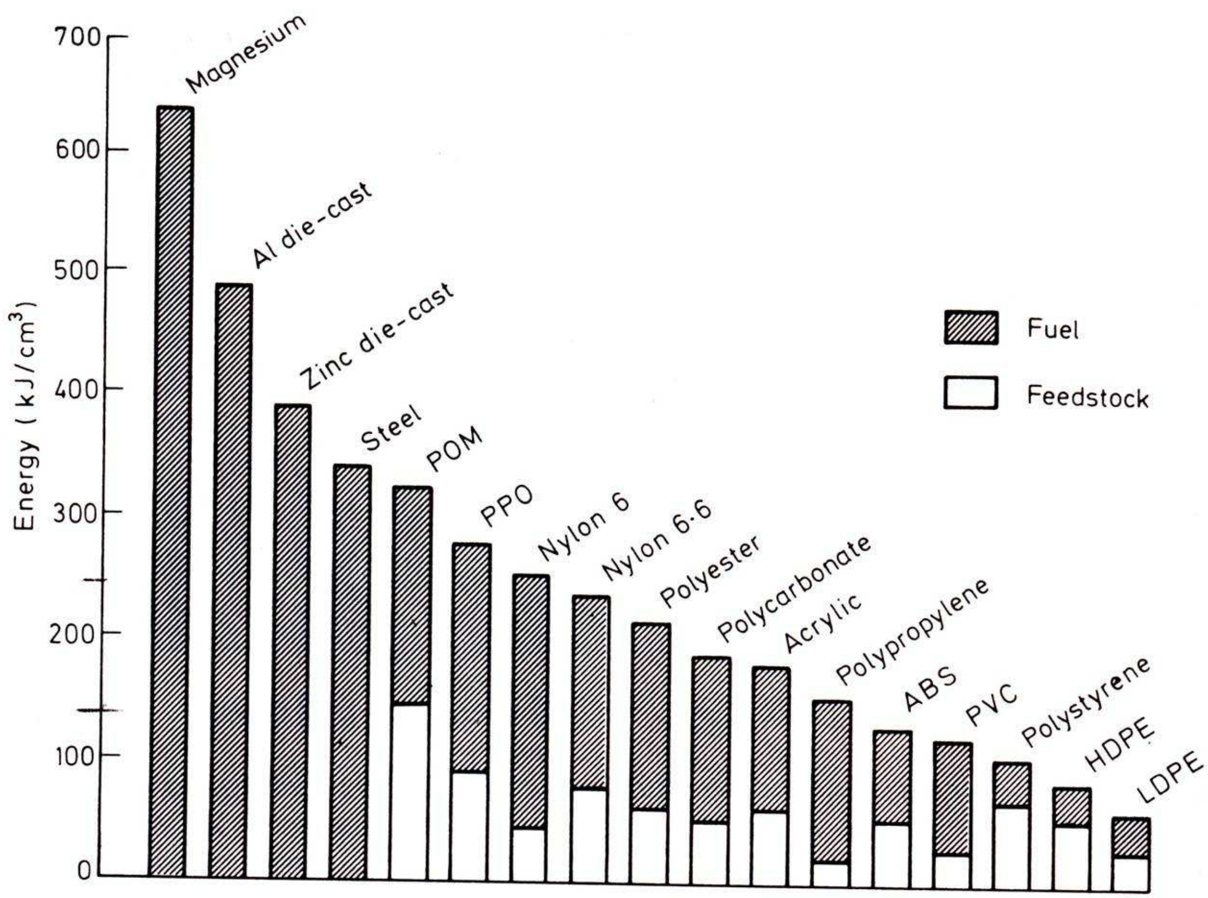


Polymer Production



General process for making plastics

energy requirements for materials production (per cm^3)



0.7 Energy requirements to produce metal alloys and plastics. For plastics the energy required to manufacture the plastic is shown separately from the fuel equivalent of the raw material.

HWK #4 Materials Production

1. Please estimate the Ecological Footprint for the production of one metric ton of aluminum. State you assumption.
2. Estimate the Second Law efficiency (η_{II}) for the Roasting and Smelting of copper sulfide ore in US Industry.
3. Estimate (η_{II}) for the final refining step for copper in US Industry.
4. Estimate the energy required to process recycled copper if you can skip the roasting and smelting process.
5. Using what we know so far, discuss the trade-offs of using aluminum Vs steel for the bodies of automobiles.