SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

Carnegie Mellon University

Titania slag smelting and calcination of crude zinc oxide: examples of processing under thermodynamic and kinetic constraints

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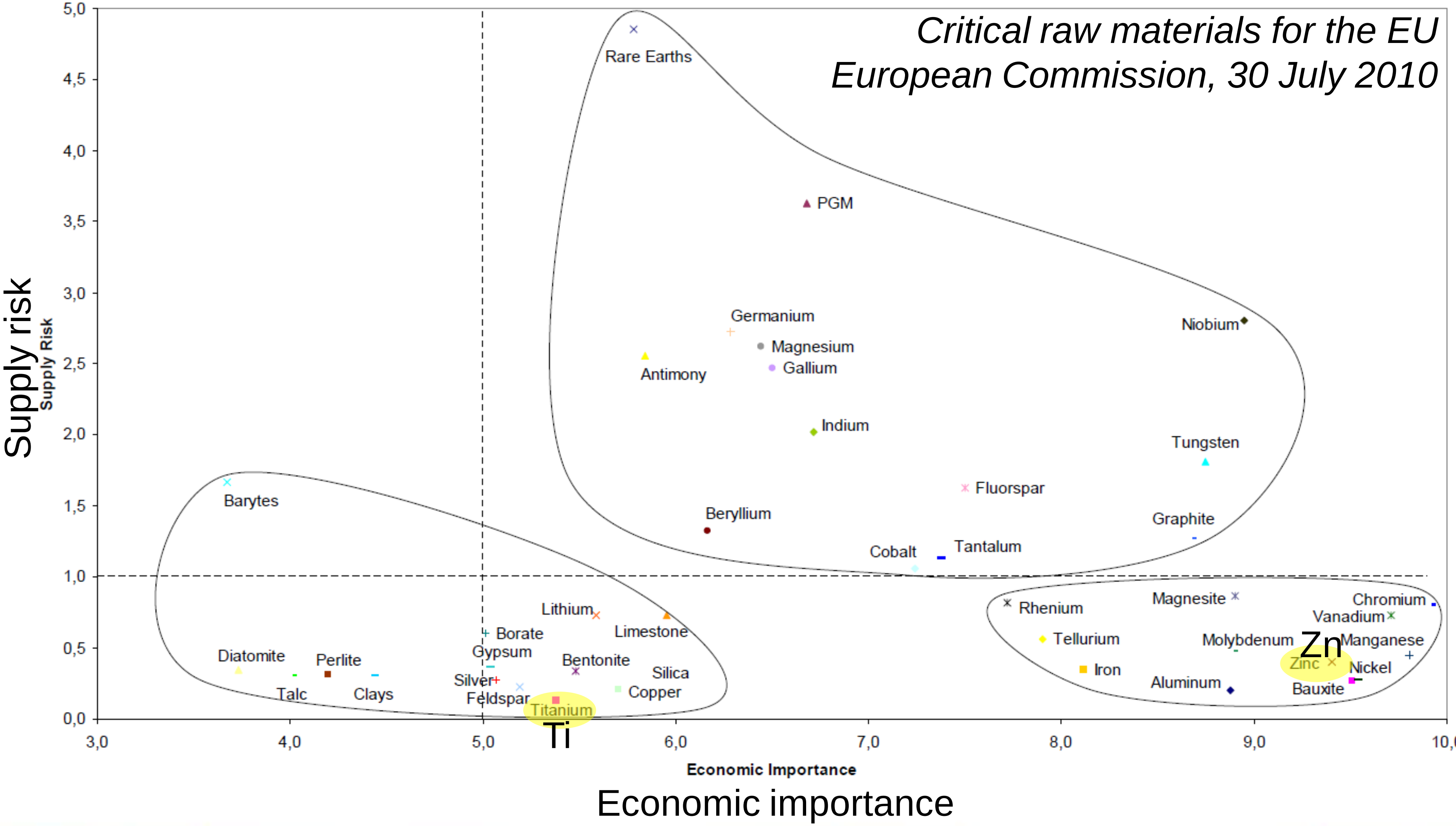
Overview

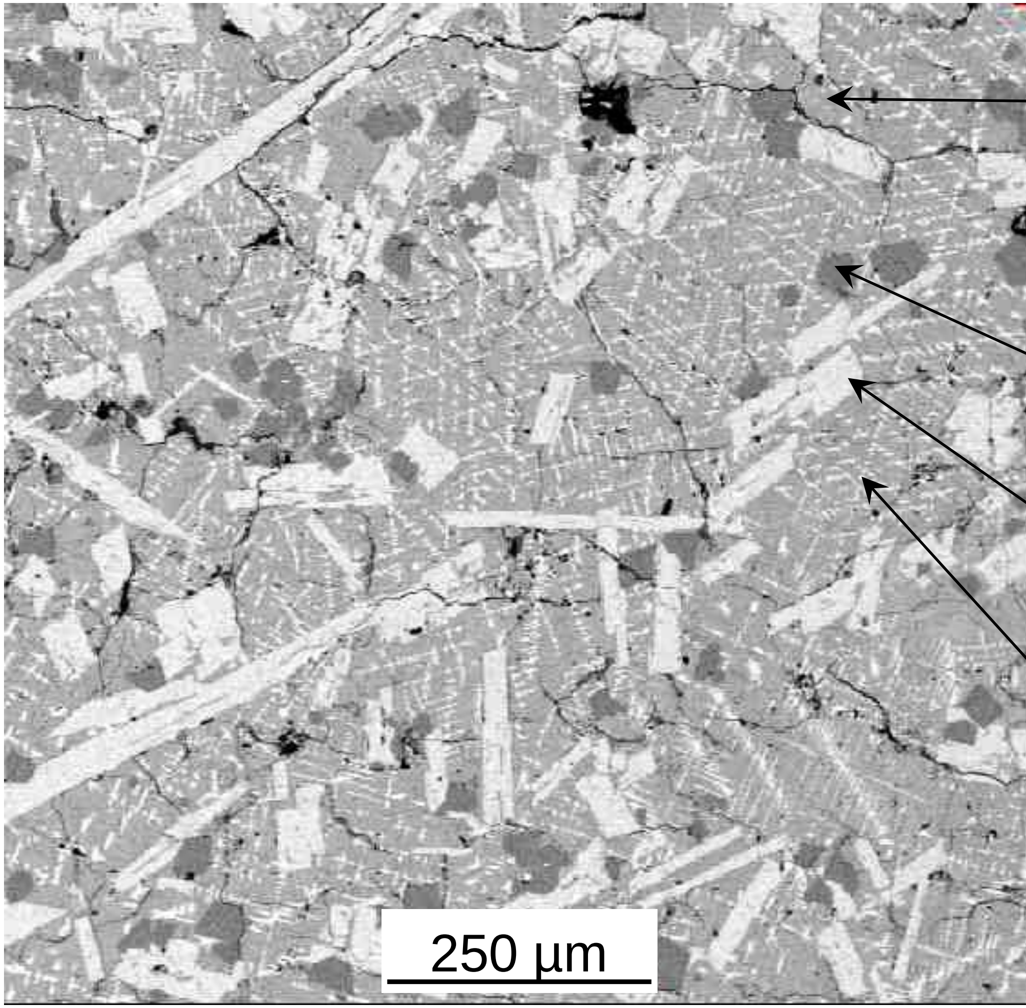
- Composition of slag and dust:
  effect on reuse possibilities
- Example 1: TiO_x-containing slags
  - Possible source of TiO_2 for pigment production
  - reuse hampered by lack of economical Ti-specific extraction route
- Example 2: Zn-containing EAF dust
  - Zn extraction by volatilization;
  - silicate / salt impurities affect calcination

Supply risk & economic importance (EU report)



Example of available slag resource (?) (Highveld Steel & Vanadium, South Africa)

Multiple phases in slag from smelting of titaniferous magnetite



Titanaugite matrix (SiO_2-Al_2O_3-CaO-MgO-TiO_2)

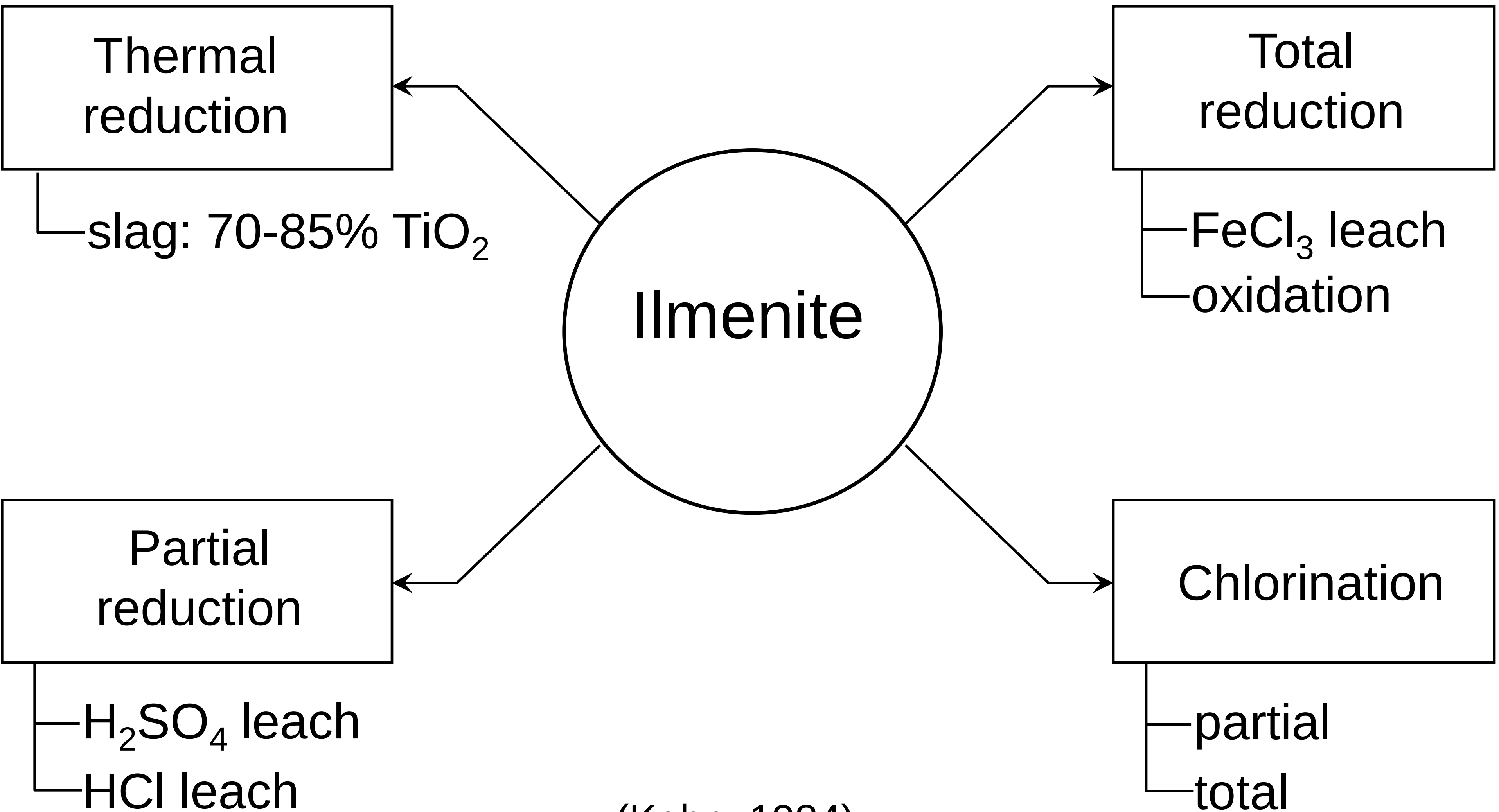
Spinel (Mg,Fe)(Al,Ti,V)$_2$O$_4$

Pseudobrookite (Ti,Mg,Al,V)$_3$O$_5$

Perovskite $CaTiO_3$

Nominal composition: 32% TiO_2, 22% SiO_2, 17% CaO, 15% MgO, 14% Al_2O_3, 0.9% V_2O_5

Currently used upgrading routes



(Kahn, 1984)

Titanium feedstock upgrading routes

- Primarily aimed at removing FeO_x by selective reduction
- Solid state reduction: Becher process
  Slag reduction: Ilmenite smelting
- *Constraints*
  sulfate process for pigment:
  TiO_x species must be acid soluble (no rutile)
  chlorination route: strict limits on CaO, SiO_2, MgO, etc.
- *Proposed* upgrading processes for complex slags (~30% TiO_x; others mainly CaO, SiO_2, MgO, Al_2O_3)

Proposed upgrading routes (1)

- Panzhihua (blast furnace) slag:
  oxidize in liquid state; perovskite ($CaTiO_3$) precipitated; crush cooled slag; recover perovskite by flotation

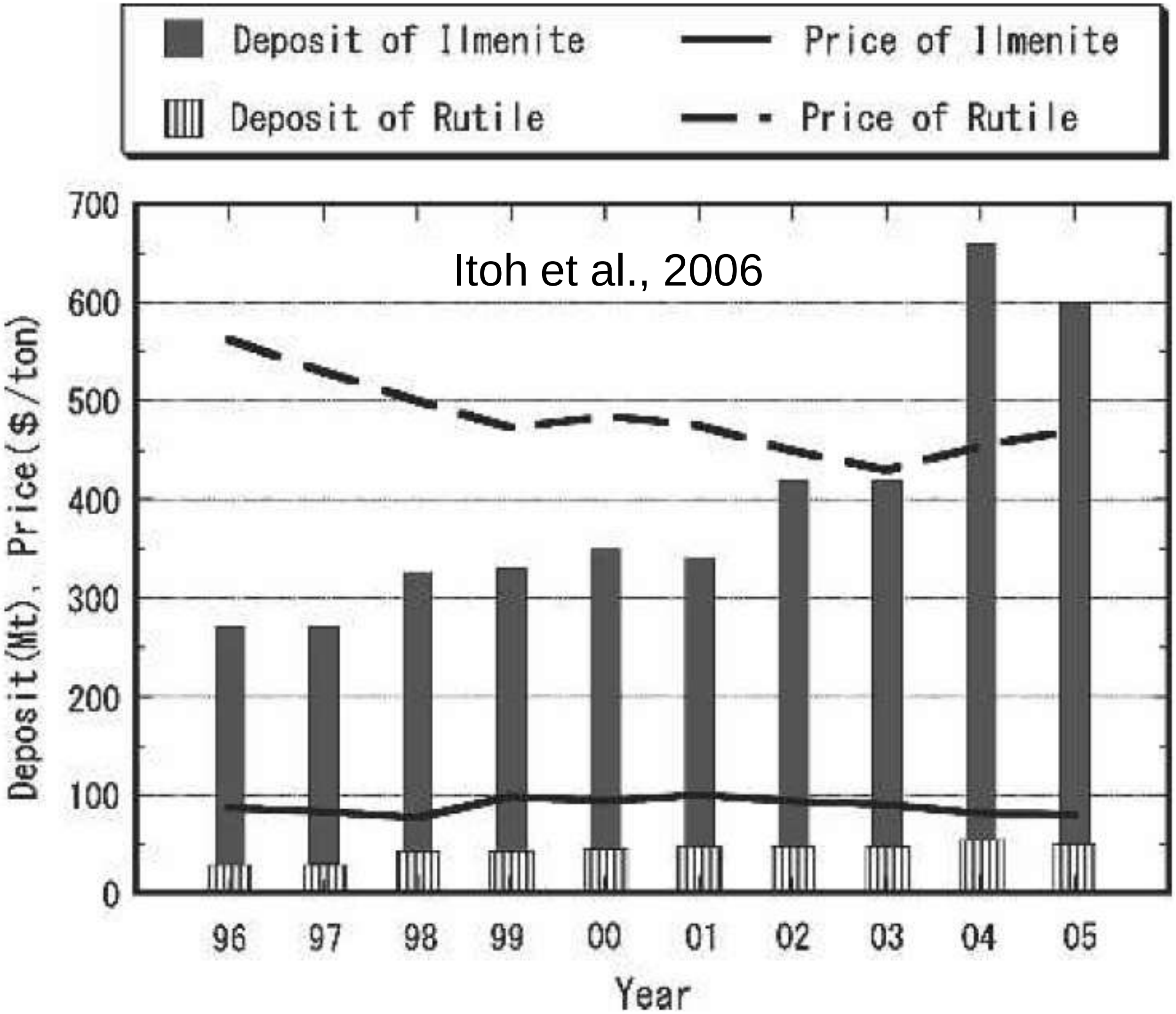
  How useful is perovskite as TiO_2 feedstock?

  Possible perovskite processing routes:
  alkali roasting + acid leaching;
  phosphate treatment; leaching calcium phosphate

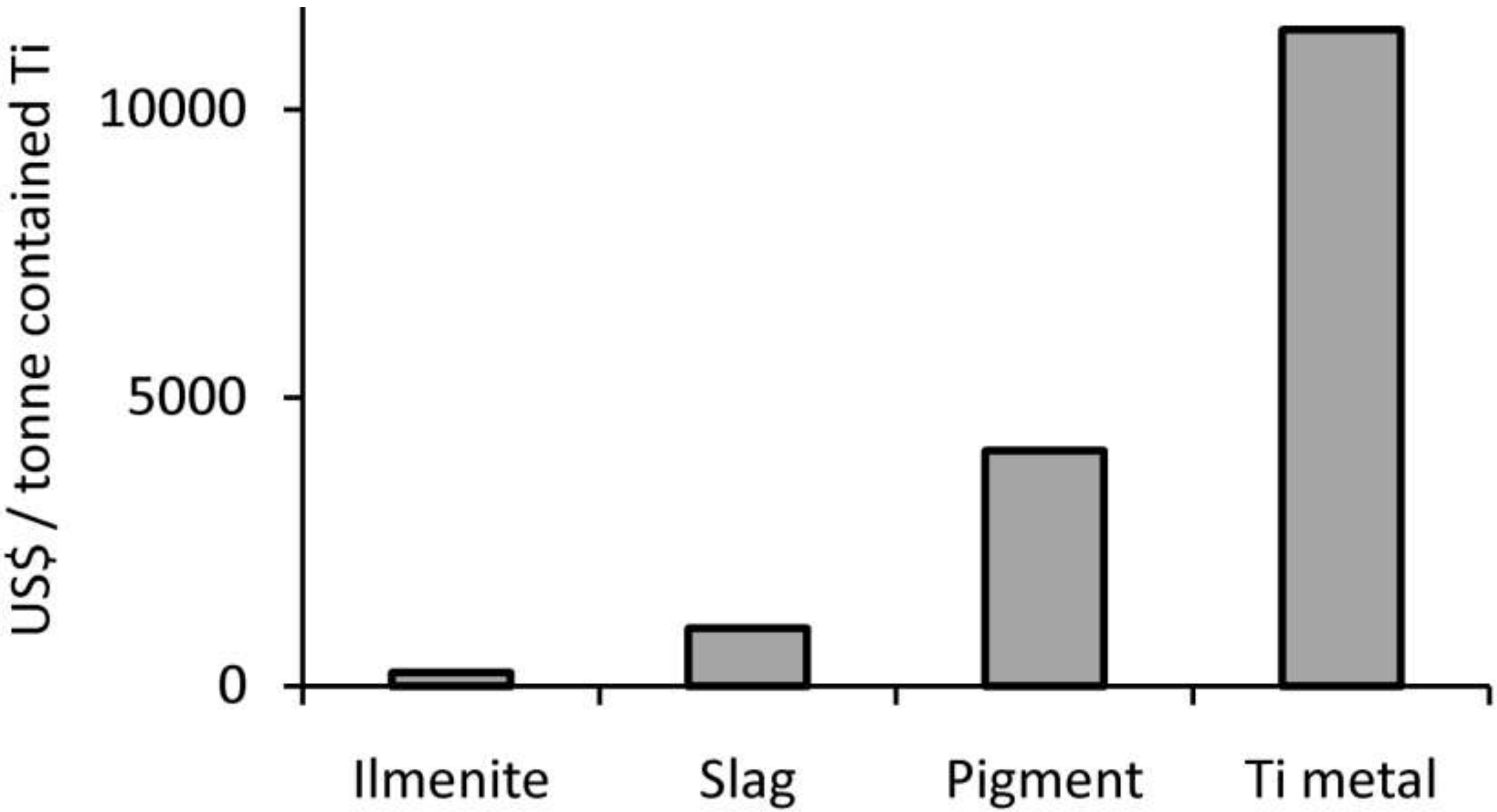
Proposed upgrading routes (2)

- Highveld Steel & Vanadium slag:
  Various processes proposed
- Nitriding slag to form TiN;
  chlorinatable at low temperature
- Sulfuric acid leaching (similar to sulfate pigment route)

Low cost of ilmenite is a major limitation



Prices of materials along Ti value chain



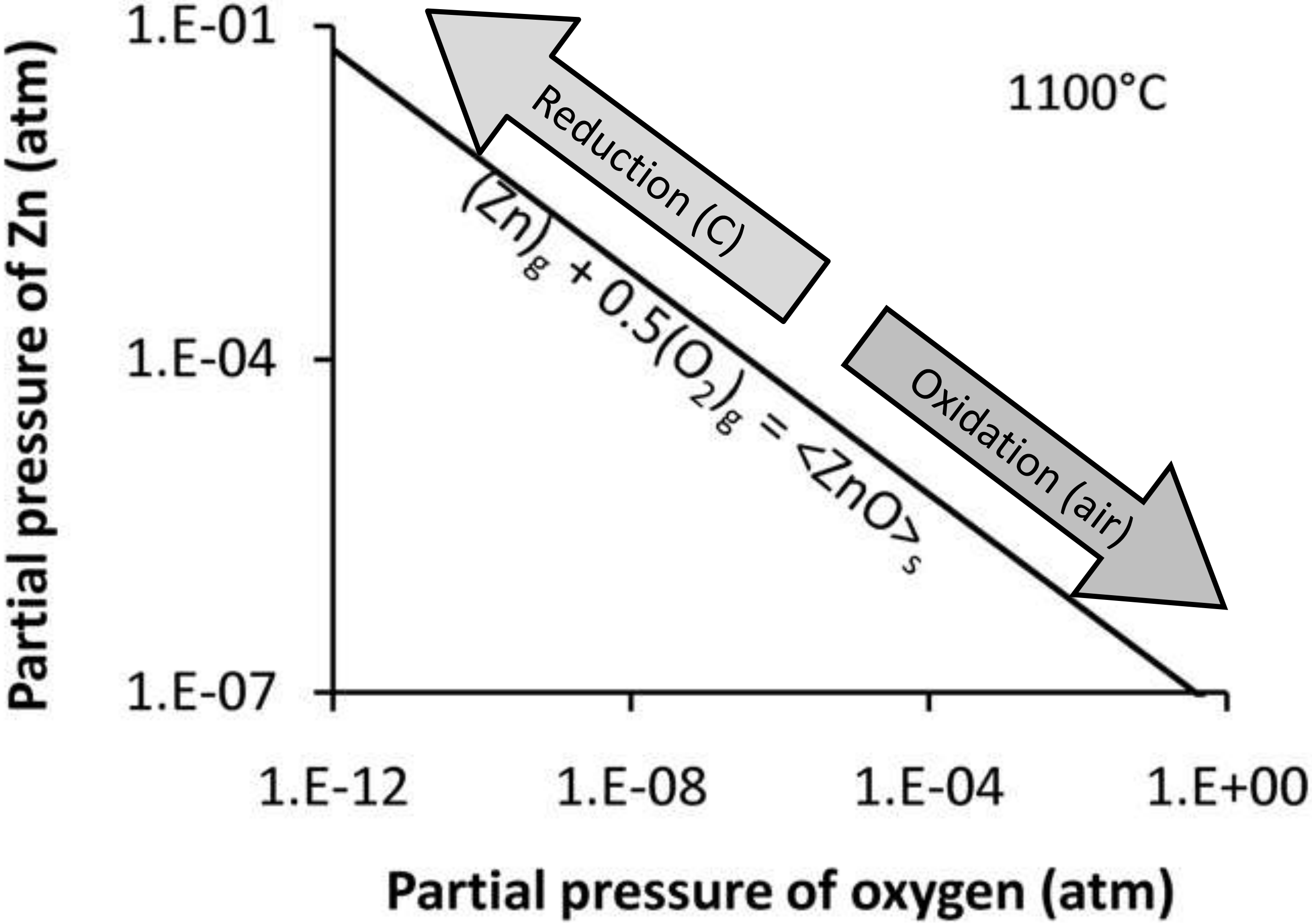
Source: US Geological Survey

Ilmenite mining operation

Recovering zinc from EAF dust

- Electric Arc Furnace (EAF) dust:
  volatile species & fines from steel scrap & slag
- Typical composition range:
  30-40% Fe, 2-5% Pb, 15-25% Zn, 1-5% Cl; 0.1-0.2% Cd
- Main zinc recovery method:
  Waelz kiln (C-based reduction); Zn fumed off

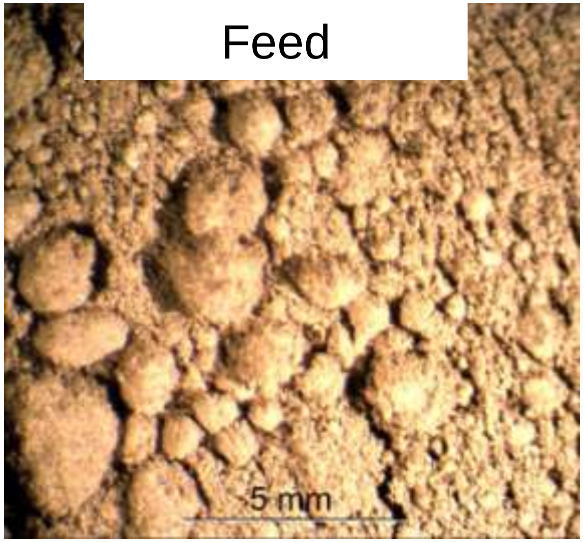
Zn extraction: manipulate p_{O_2}

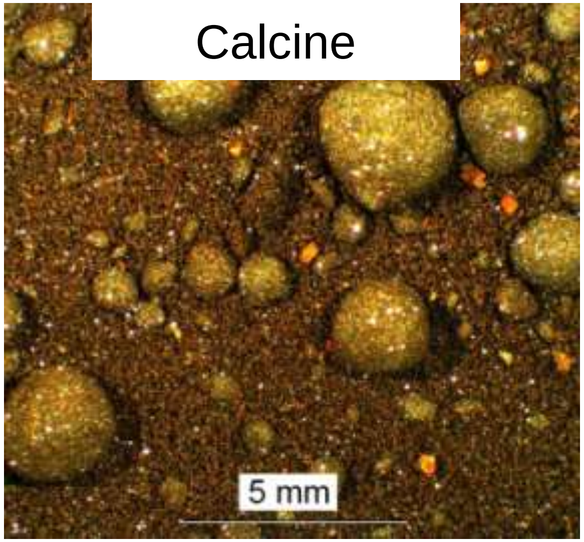


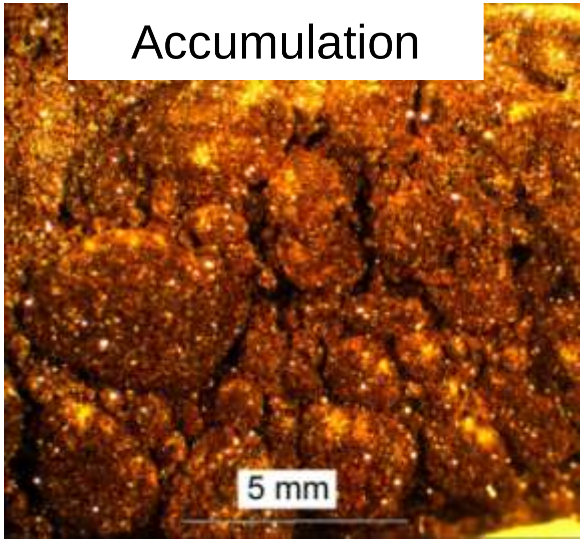
Two-stage Waelz kiln process

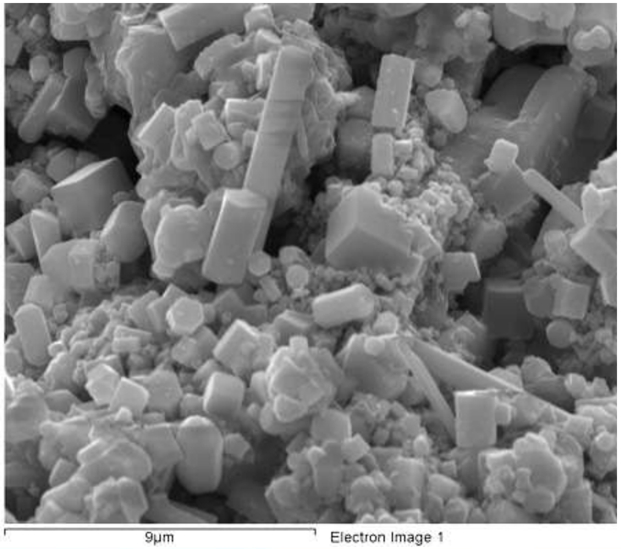
- First stage: Zn fumed off (with other volatiles); oxidized to ZnO
- Second stage: crude zinc oxidized by calcination
  - chlorides (Pb & Cd) removed; also K_2SO_4
  - oxidizing conditions
- Calcination in rotary kiln; accretions form
- Temperature ~1200°C

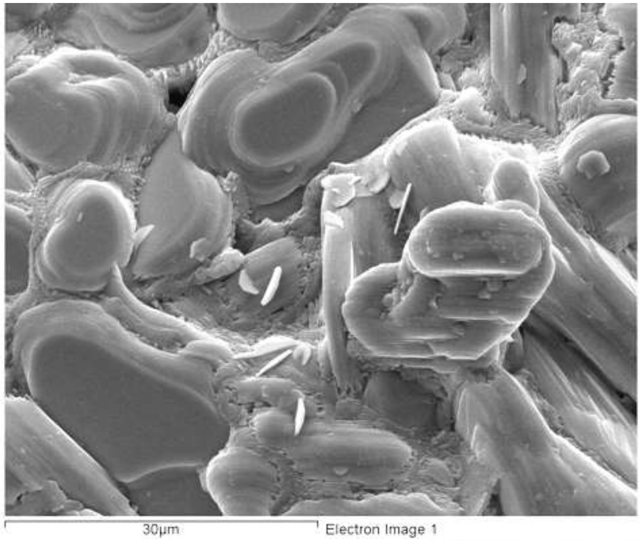
Change in zinc oxide upon calcination



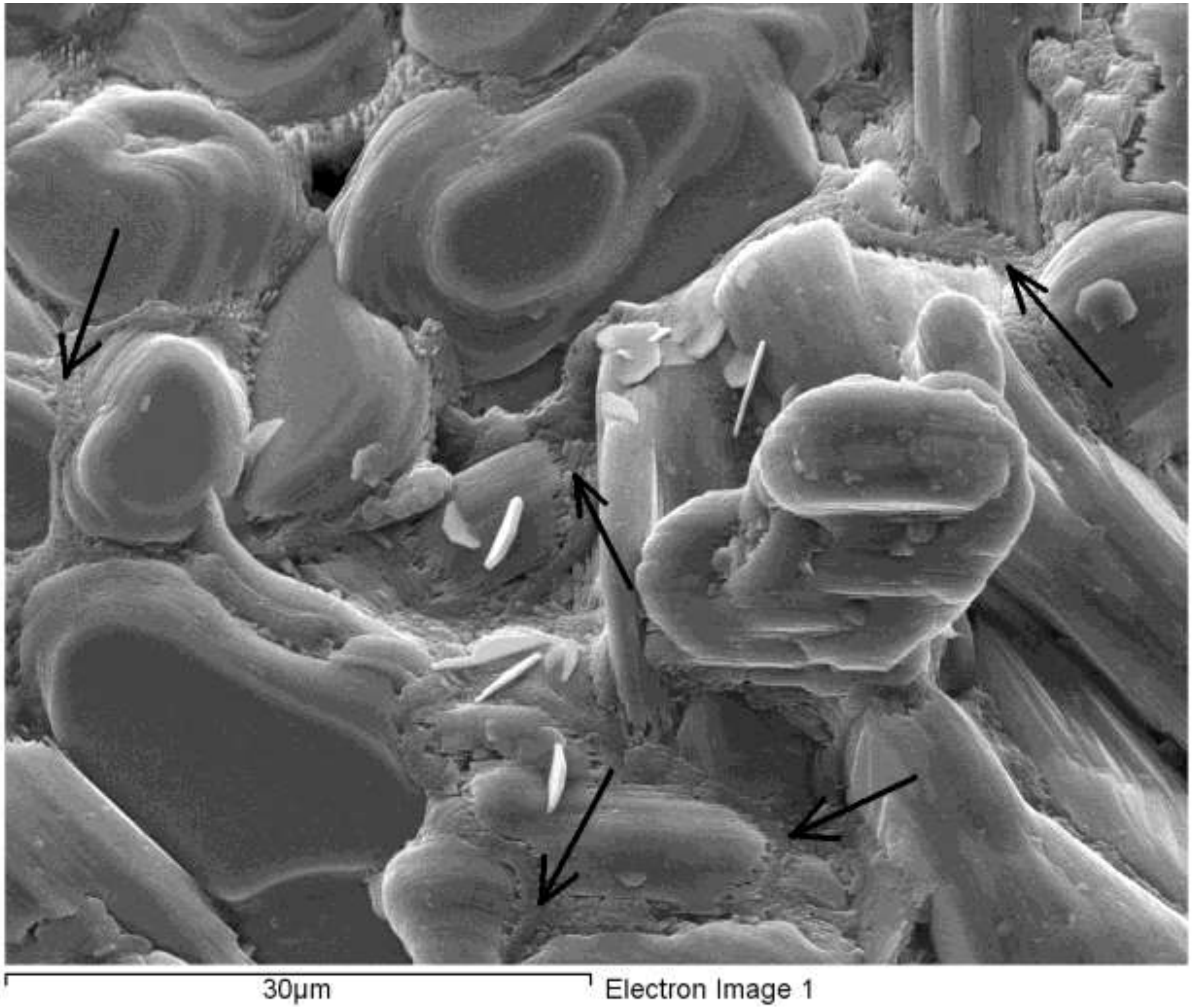








Binding phase between ZnO platelets



Binding phase: silicate

Molar ratios:

$CaO/SiO_2 \approx 1.5$

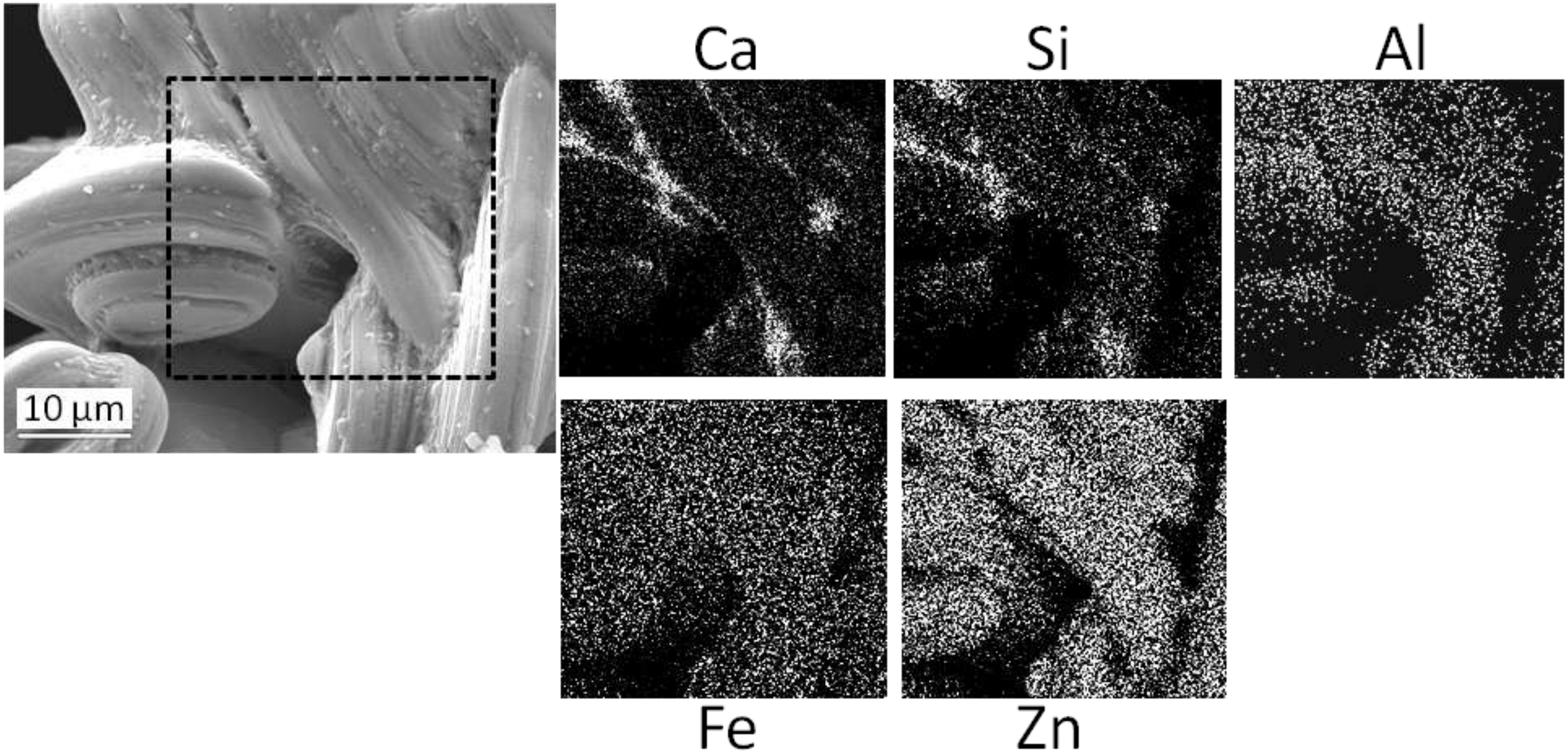
$AlO_{1.5}/SiO_2 \approx 0.04$

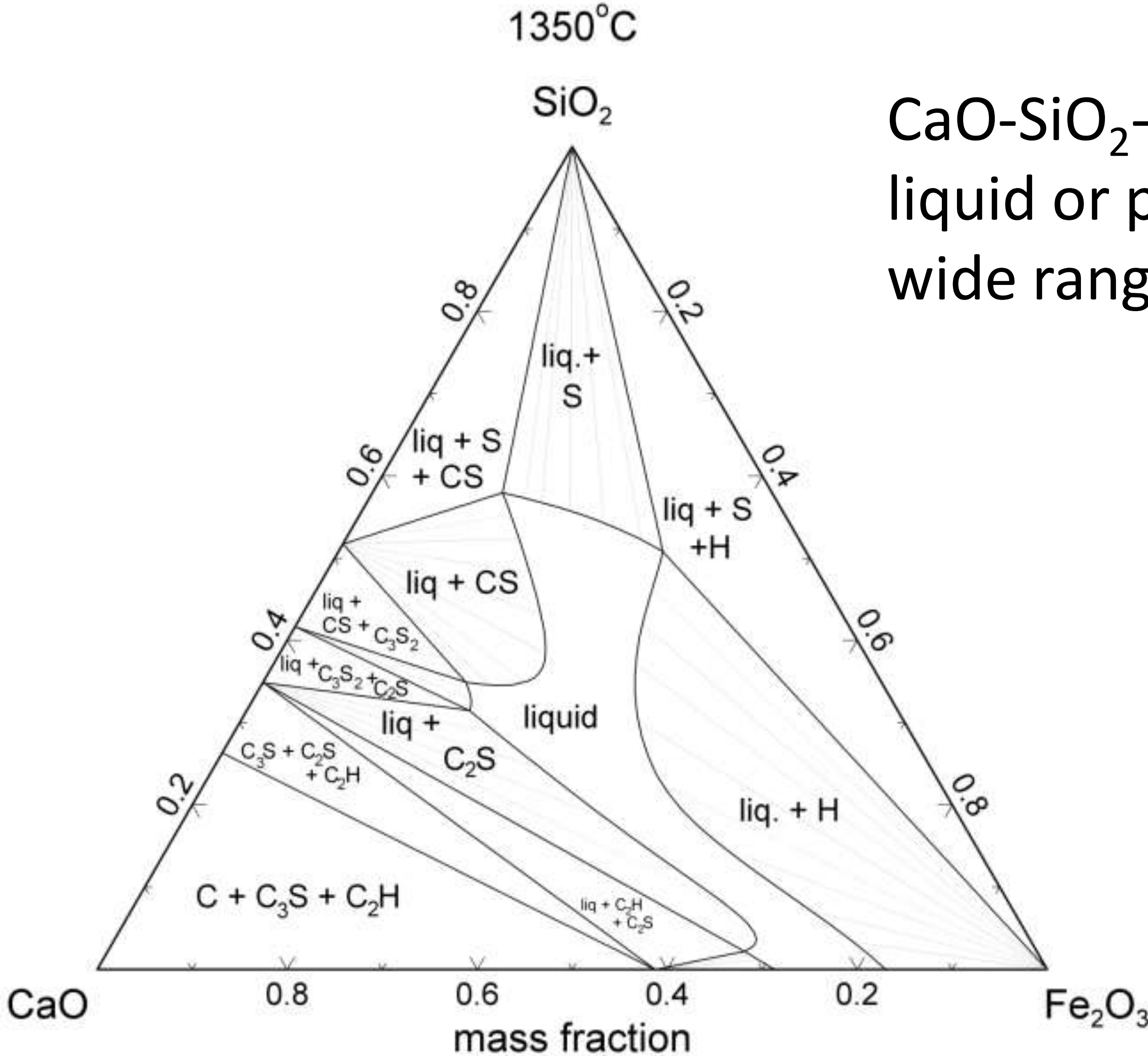
$FeO_x/SiO_2 \approx 0.2$

$ZnO/SiO_2 \approx 1.2$

(Crude zinc oxide contains ~1% SiO_2)

Binding phase: EDS element maps

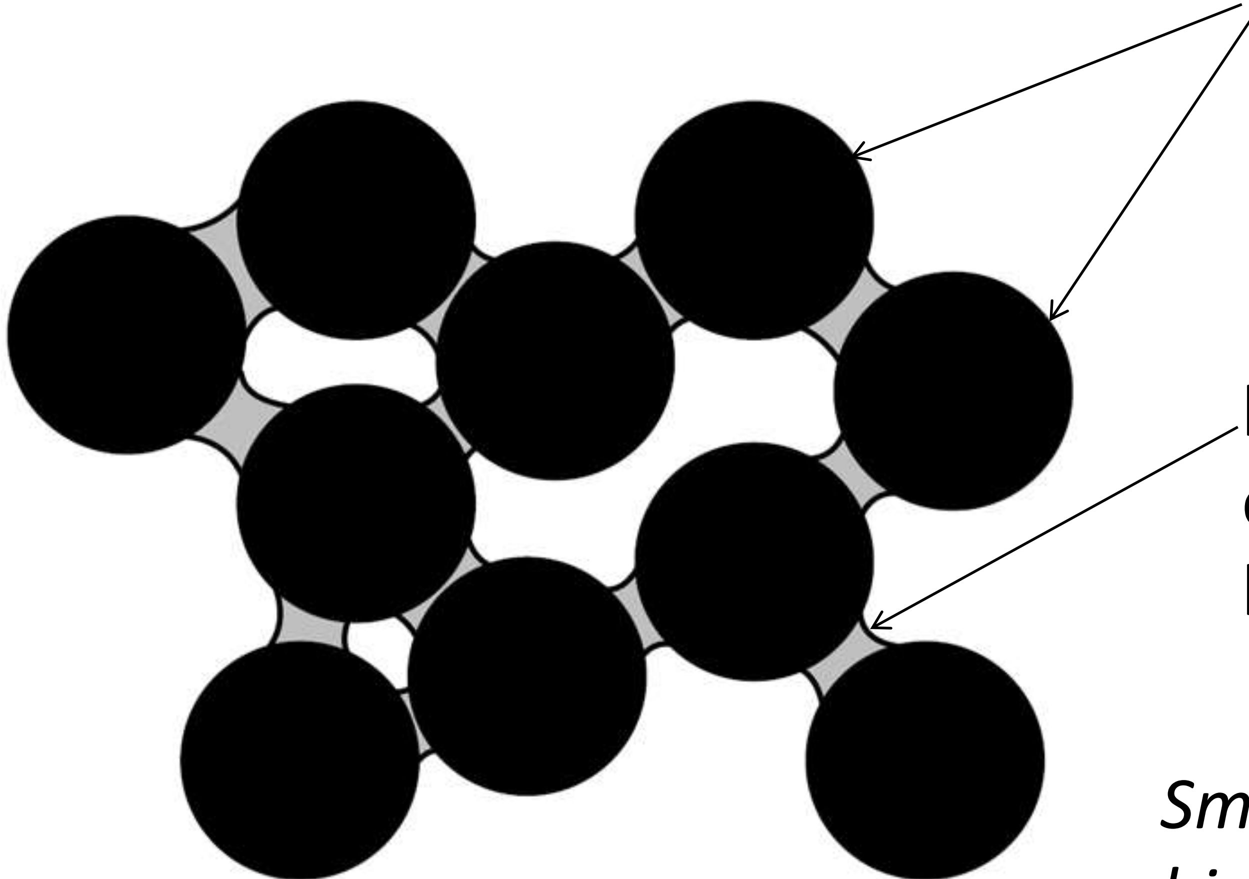




CaO-SiO_2-Fe_2O_3:
liquid or partially liquid over wide range of compositions

(FactSage)

Wet granular solid



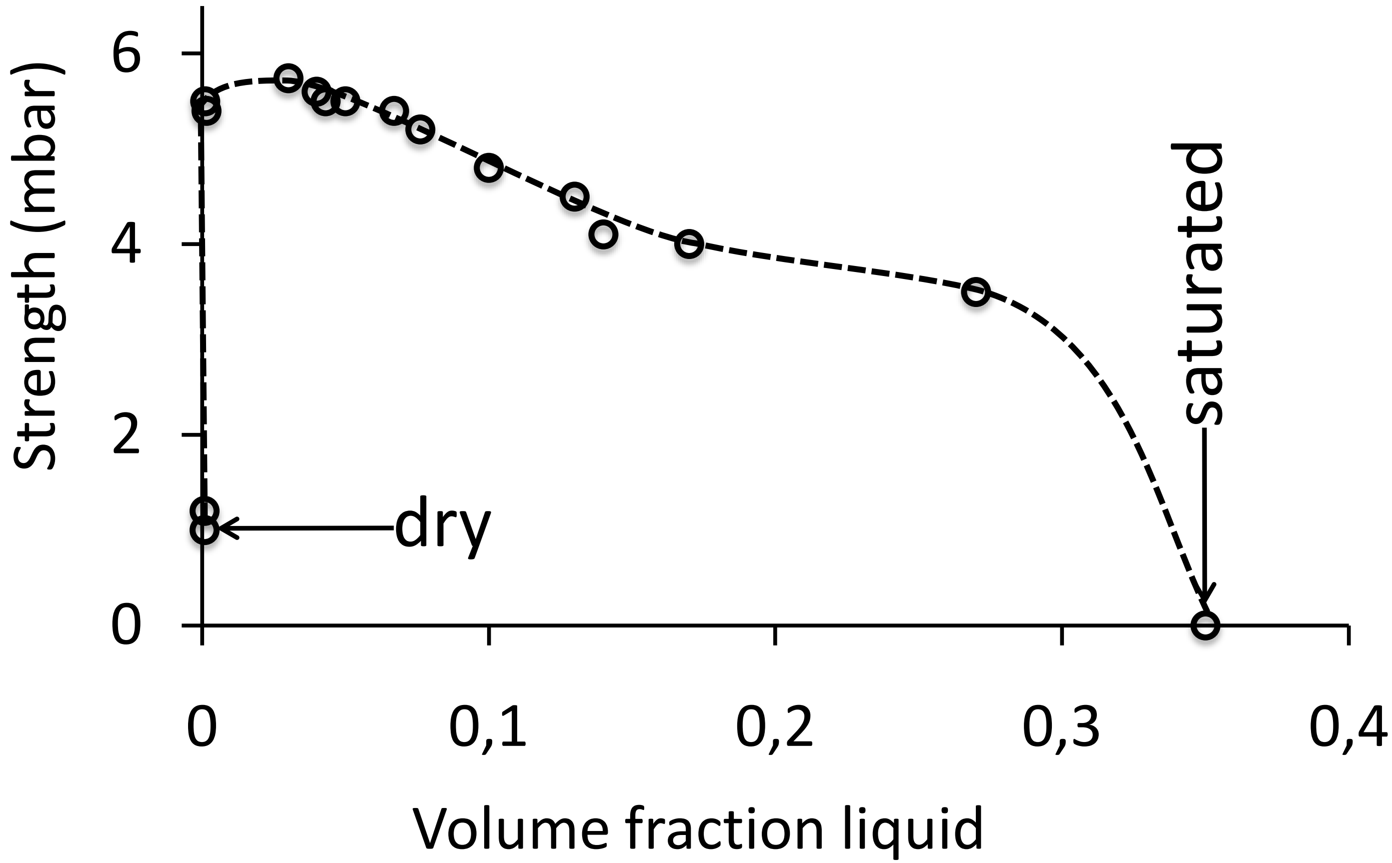
(Mitarai & Nakanishi: *EPL*, vol. 88 [2009], 64001)

Small amount of liquid binds solid particles together: wet sand is stronger than dry sand

Possible ways to manage accretions

- Live with the problem
- *Increase* the amount of liquid:
  operate the kiln more like a cement kiln
  - Cement kiln:
    Forms coating in burning zone,
    but coating reaches steady state thickness
    - amount of liquid ~ 25-30%

Mixture with more liquid: softer & less likely to accumulate



(Fournier *et al.*, 2005)

Conclusions

- Complexity of slags and dusts strongly affect difficulty & cost of purification / extraction
- Examples:
  TiO_x-containing slags
  - Ti-specific extraction routes: acid leaching; chlorination

  Zn-containing dusts
  - Small (few %) if silicates form binding phase during 1200°C calcination