# Modelling non-ferrous processes
## and the importance of the gas phase

dr. Sander Arnout, dr. Els Nagels

InsPyro

# 5 years InsPyro: references

**Lead**

RECYLEX, FMM, campine recycling, BERZELIUS METALL, BBH STOLBERG, STCM

**Zinc**

ERAS, nyrstar Resources for a changing world, recytech Valorisation du zinc

**Steel**

aperam, Nedstaal, ASCOMETAL, LSW

**Foundry**

MAGOTTEAUX, Allard EUROPE, Dovre

**Various**

SADACI, RIO TINTO MINERALS, SMS SIEMAG SMS group

ROCKWOOL, Heraeus Electro-Nite

# InsPyro approach

= Knowledge centered approach

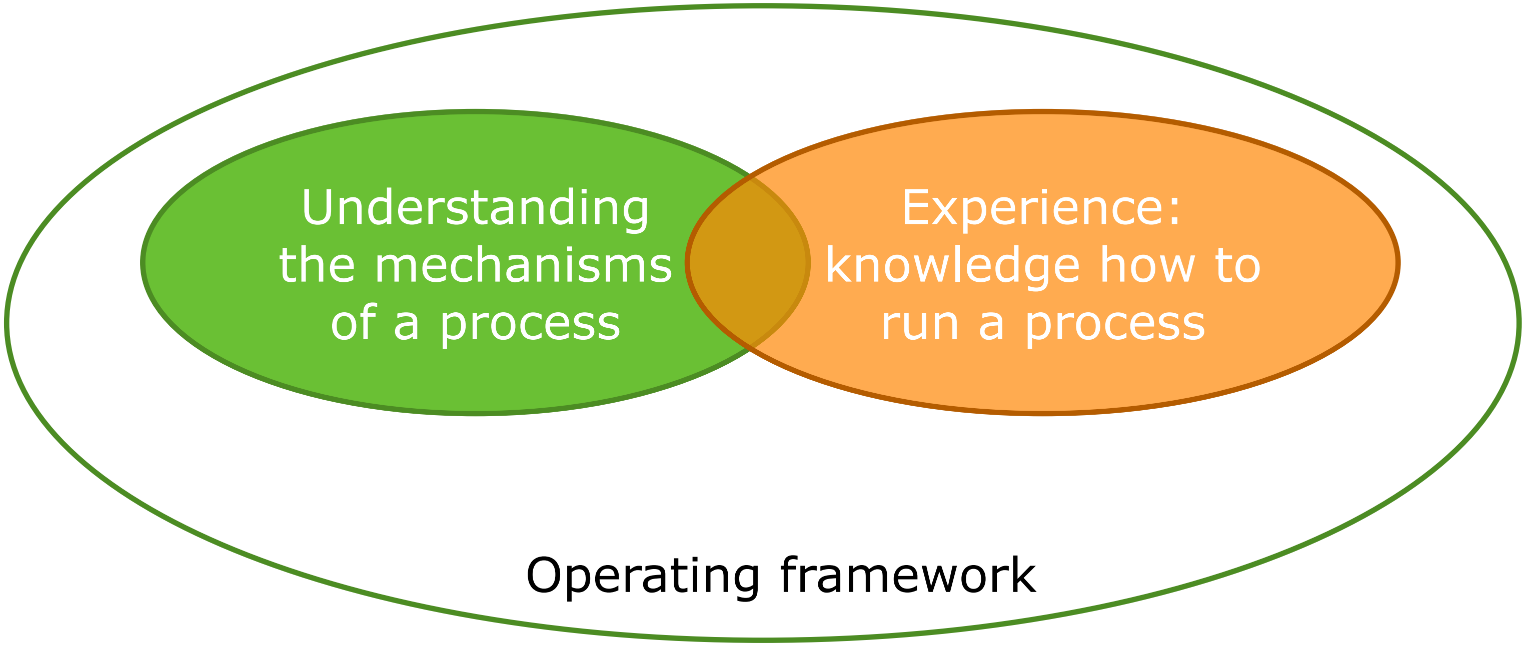
**Understanding the mechanisms of a process**

- Useful to run a process
- Control depends on model
- Changes are based on physics, thermodynamics…
- Mechanisms get unraveled
- Transferrable

**Experience: knowledge how to run a process**

- Essential to run a process
- Control depends on individual
- Changes based on trial and error
- Mechanisms unclear
- Experience transfer is difficult

# InsPyro approach



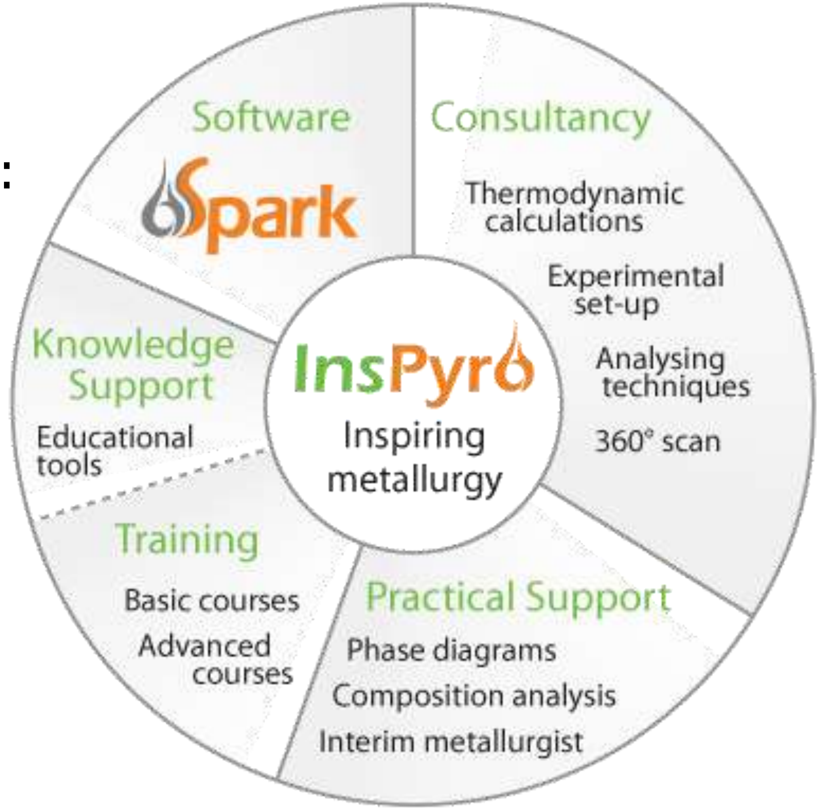
# Knowledge management

- Knowledge in the heads of people is the most readily applicable, but the most volatile:
  - People leave, retire, are on holiday
  - Intuition and feelings may be working most of the time, but may never be thoroughly checked/understood
- Need to develop concepts which are more easily transferable:
  - Define rule of thumb based on mechanisms
  - Actual process model can be useful for complex interactions
  - Summaries, concepts, hypotheses can already be much more tangible than feelings, and can be validated
  - Provide a basis for decision making, experimenting, education of operators

# Mission: « Inspiring Metallurgy »

InsPyro improves existing high-temperature processes
develops new sustainable processes

Full circle approach:



# Process development

- Stepwise process:
  1. Concept from literature or experience
  2. Process model to define expected working area
  3. Lab or pilot scale experiments
  4. Validate process model
  5. Scale-up or adjustments

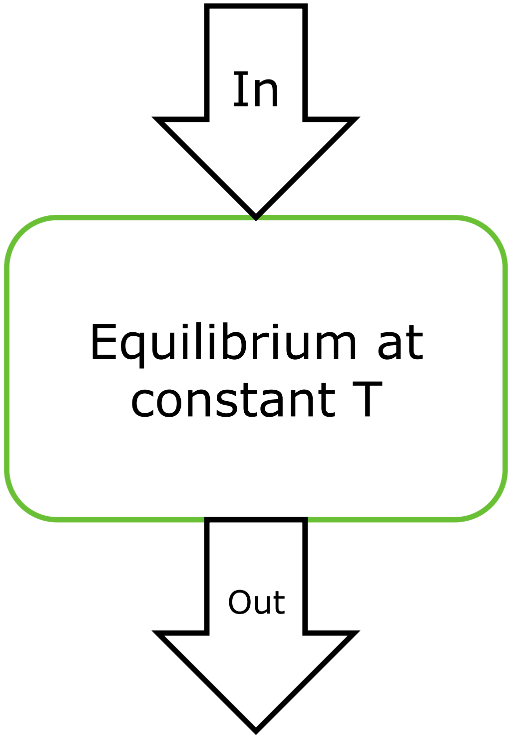
- Nobody will develop a new process without a model
- Yet we run several existing processes without an explicit model

# Process improvement

- Similar approach as for development
  - Literature review
  - Advantage: also process data available
  - Construct process model
  - Verify process model with experience
  - Define conditions which are expected to improve the process

  - Use process as test facility

# Simple process model




Mainly a mass balance with an indication of heat requirements for one operating point

No need to model all possible reactions!

# Integrated in charge calculation

Spark

## CHARGE CALCULATION FOR LEAD RECYCLING (SIMPLIFIED)

InsPyro

| Selection of raw materials | Amount (kg) | Water content | Dry weight | Composition of dry fraction: Pb | Fe | Sb | Ca | Si | Al | Na | S | O | C | organics | Mass balance: Pb | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Paste | 1000 | 8.0% | 920 | 90.0% | | | | | | | 3.0% | 7.0% | | | 828 | 0 |
| Plates | 1000 | 2.0% | 980 | 97.5% | | 1.0% | | | | | 0.5% | 0.5% | | 0.5% | 956 | 0 |
| Coke | 25 | | 25 | | | | 0.5% | 1.0% | 1.0% | | | | 95.0% | | 0 | 0 |
| Lime | 5 | | 5 | | | | 71.5% | | | | | 28.5% | | | 0 | 0 |
| Iron turnings | 70 | | 70 | | 100.0% | | | | | | | | | | 0 | 70 |
| Soda ash | 20 | | 20 | | | | | | | 43.4% | | 45.0% | 11.0% | | 0 | 0 |

**Model estimation: using thermodynamic calculations**

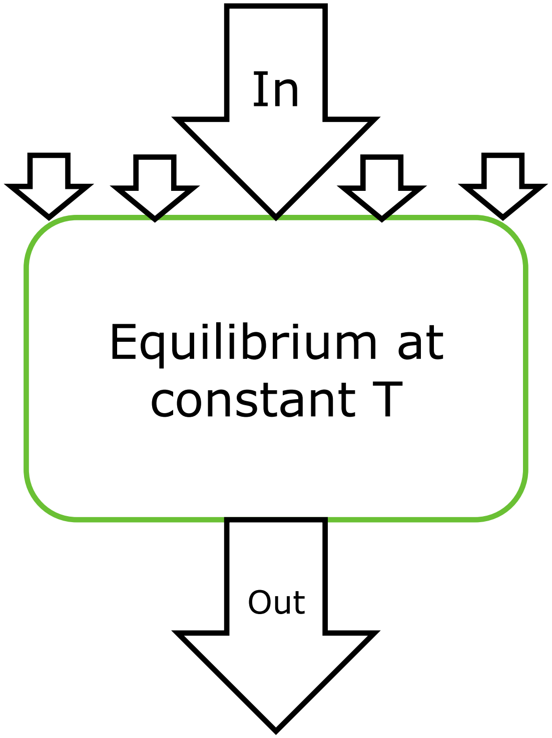
Temperature 1100 °C — Heat need/input DEMO kWh — Recalculate — Ready

| | Total weight (kg) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Bullion | 1738 | Pb | Sb | S | O | | | | |
| | | 99.1% | 0.6% | 0.32% | 0.00% | | | | |
| Slag | 14 | CaO | SiO2 | FeOx | Na2O | Na2SO4 | PbO | Al2O3 | ... |
| | | 32.8% | 37.4% | 3.9% | 22.5% | 0.2% | 0.1% | 3.1% | |
| | Solid phases: 0% | | | | | | | | |
| Matte | 159 | Fe | S | O | Na | Pb | | | |
| | | 40.7% | 16.2% | 7.3% | 3.8% | 32.0% | | | |
| Gas | 100 | SO2 | | | | | | | |
| | | 0.04 kg | | | | | | | |
| Other phases | 8 | kg Fe excess | | kg C excess | | | | | |
| | | 0 kg | | 0 kg | | | | | |

| Composition of raw materials: Raw material name | Water fraction | Analysis dry fraction: Pb | Fe | Sb | Ca | Si | Al | Na | S | O | C | organics |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Plates | 2% | 97.5% | | 1.0% | | | | | 0.5% | 0.5% | | 0.5% |
| Paste | 8% | 90.0% | | | | | | | 3.0% | 7.0% | | |
| Cable strippings | | 90.0% | 5.0% | | | | | | | | | 5.0% |
| Lead ingots | | 99.9% | | 0.1% | | | | | | | | |

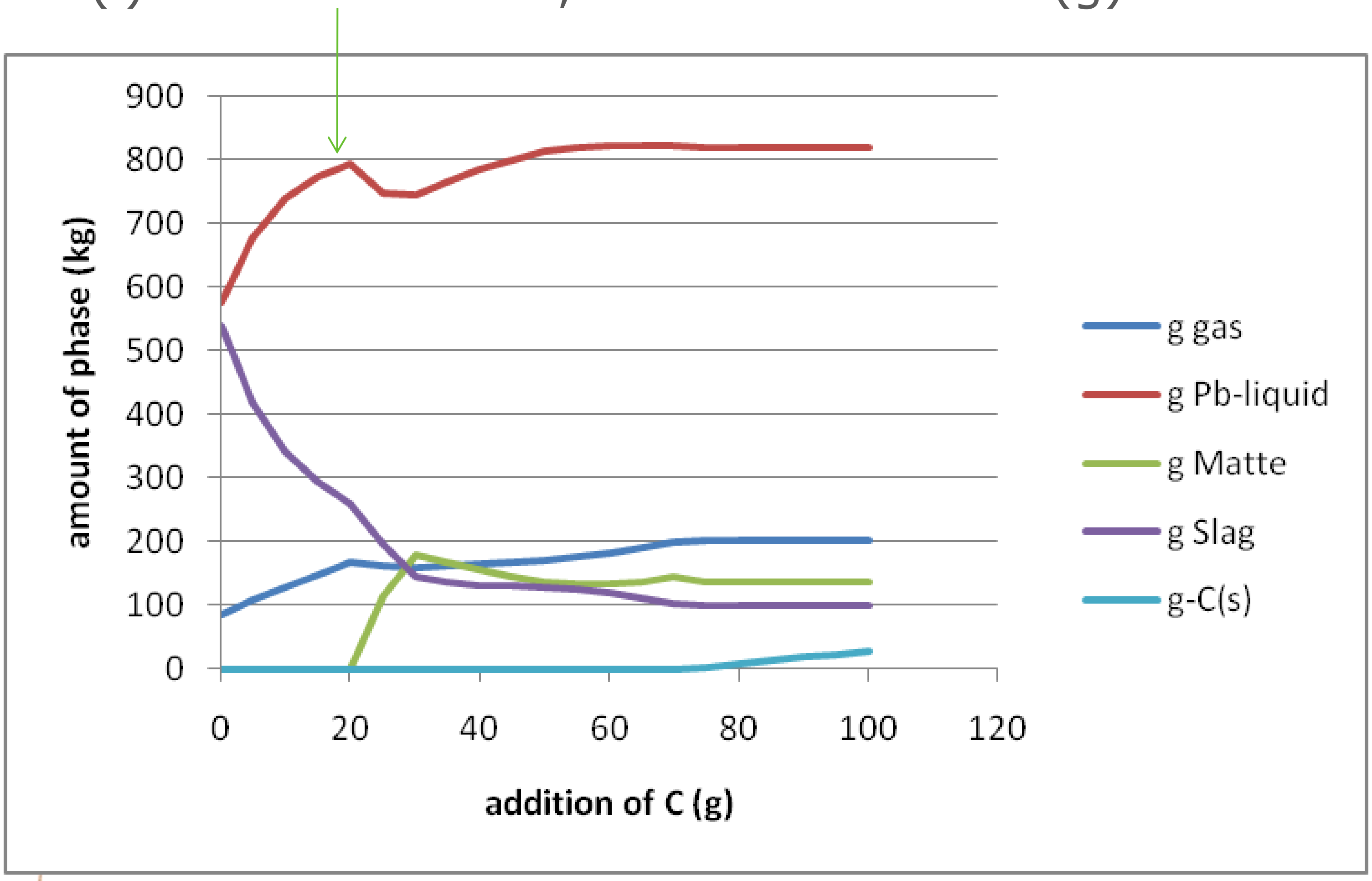
charge | slag properties | pricing | phases | parameters

# Stepwise simple process model



# Process modelling – Pb recycling

- Effect of carbon on Pb recycling with $CaO-FeO/Fe_2O_3-SiO_2$ slag
- High Pb(l) at low reduction, but S-rich and PbS(g) losses



# More advanced process model

- Take into account non-equilibrium effects
  - Assume that only a part of the system reaches equilibrium
- Different operating points in a process
  - Split the model for different zones

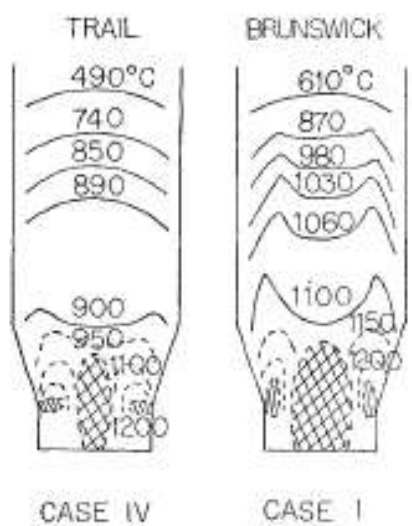
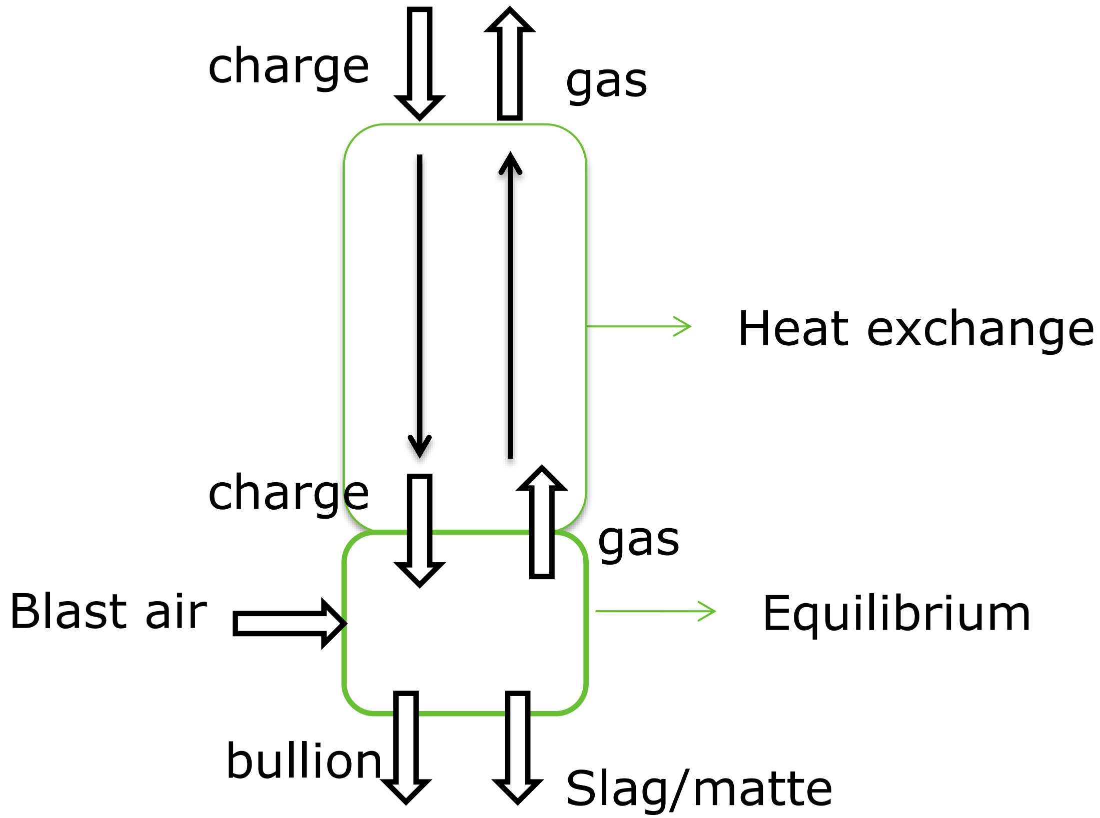



Fig. 13—Proposed isotherms and "dead man" in lead blast furnaces
Legend: ——— calculated isotherms, - - - - visualized isotherms.

Not a single operational point, but the conditions change continuously over the height of the blast furnace
- Kinetics limit reactions in cold zone
- Equilibrium can be assumed in hot part

**Source**: Chao, Met. Trans.B, 1981

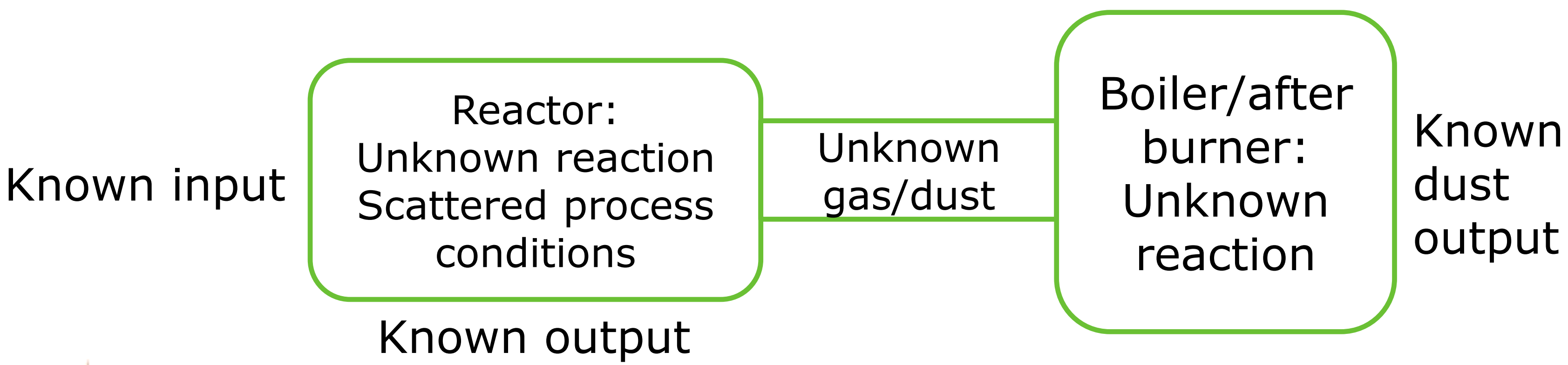
# More advanced process model




Especially the heat balance gets more realistic by implementing preheating

# Advantages of a model

- For a continuously running high-temperature plant
  - Noise causes scatter on process data, so difficult to learn from these data
  - Data over a year basically gives few average working points, despite measuring every second/hour/day
  - Experiments can be risky or expensive, certainly time consuming
  - Additional data can be collected at a single point in time but a framework is needed to do the interpretation



# Experimental set-ups

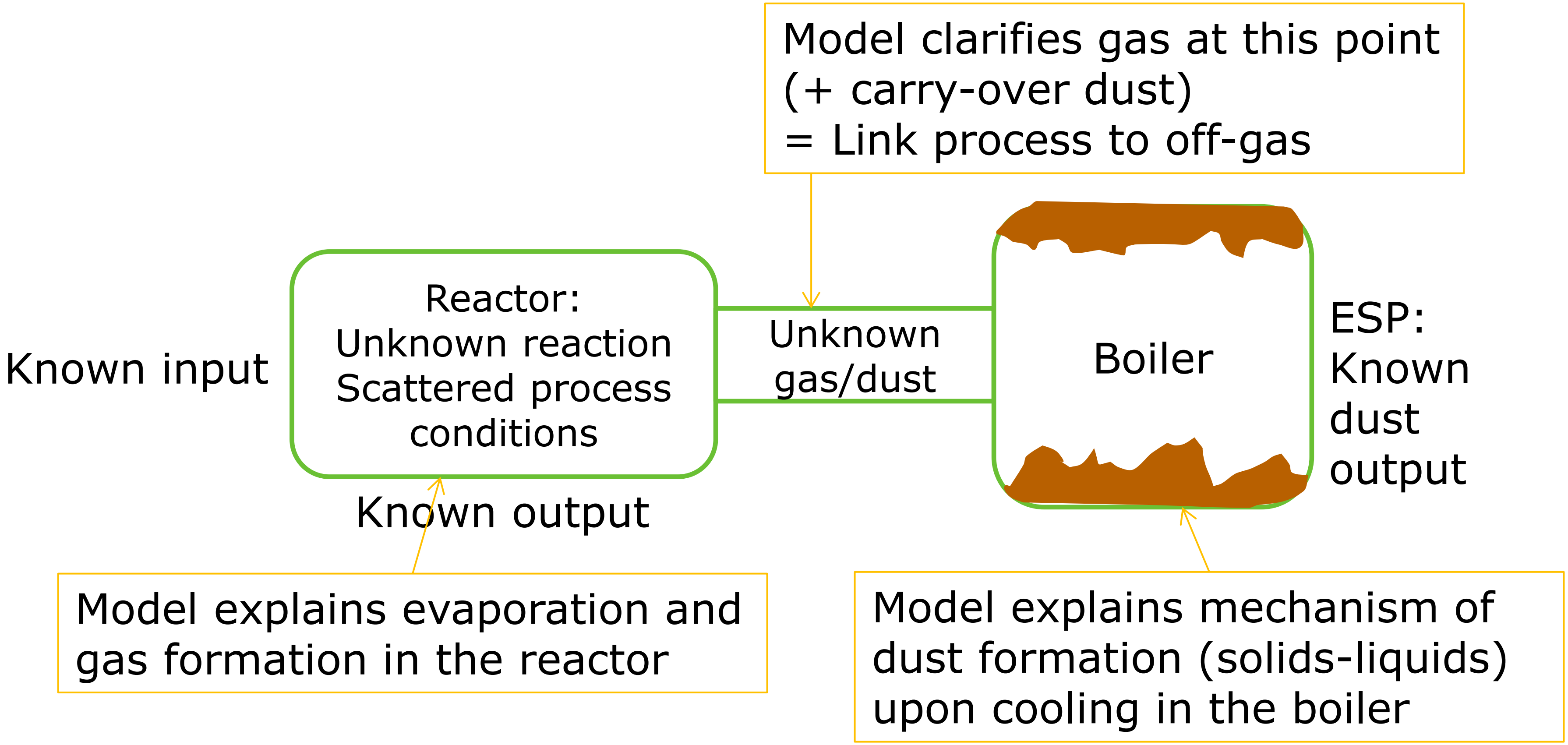
- Lab scale can give very relevant information, but not process information
- Ask a very well defined subquestion
  - Measure solubility of a certain element in slag
  - Find melting point of a matte
  - Reductive power of carbon materials
  - Maximum separation efficiency of a dross
  - Evaporation losses upon holding at high T for certain time
  - ...

# EXAMPLES OF THE ADVANTAGES OF A MODEL

# Accretion formation

- First step: characterizing the accretion
- Second step: validate with framework and look for solutions
  - Define hypothesis for accretion formation mechanism
  - Can the compounds be avoided by changing the process conditions?
    - Temperature
    - Atmosphere
    - Additions
  - Is the accrection inevitable with the current mix, but linked to certain raw materials?

# Accretion formation



# Changing raw materials

- Can they be treated similarly as known materials?
  1. Characterization: not only composition but also phase structure
  2. Feeding into model
  3. Literature may give additional guidelines

# Refining process optimisation

- How close is the refining process to the thermodynamic optimum?
  - Additions
  - Final purity of the lead
  - Temperature

1. Analysis of the dross
   - Formed phases
   - Lead losses: entrapped or chemically bound
2. Verification with thermodynamic model
   - Effect of input composition
   - Influence of temperature
3. Define optimisation opportunities

# Not everything fits in a single model

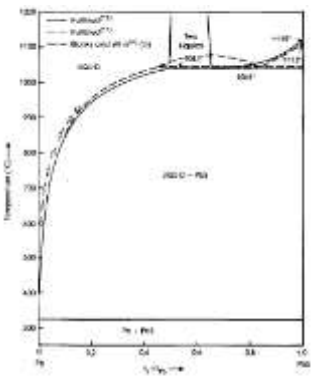
- The first version of a model can not explain everything
  - Kinetics
    - Heating time (linked to enthalpy, but also shape etc.)
    - Reaction time (mixing, settling,...)
  - Undescribed thermodynamics (compounds, rare elements)

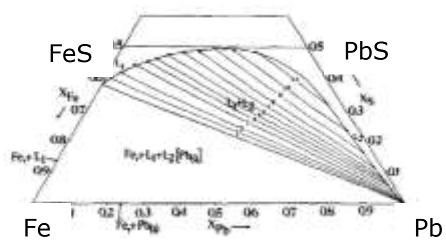
- All these aspects can also be modelled, but require a much larger effort
  - CFD
  - Empirical models based on lots of data
  - Thermodynamic database construction
  - Link to materials properties

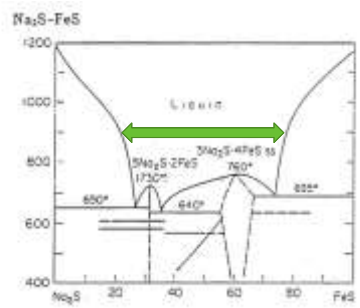
Open to partnerships!

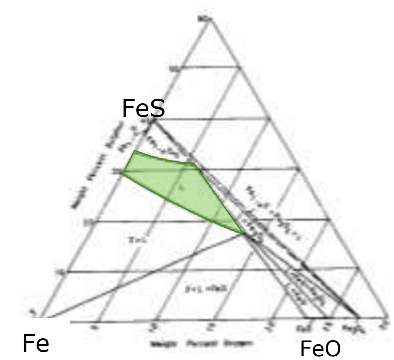
# Thermodynamics of the matte

- InsPyro has constructed a model for the matte:
  - Pb-Fe-S-O-Na system at sulphur rich side
  - Diagrams in literature are limited and several interactions have to be “guesstimated”
  - See presentation GTT2013



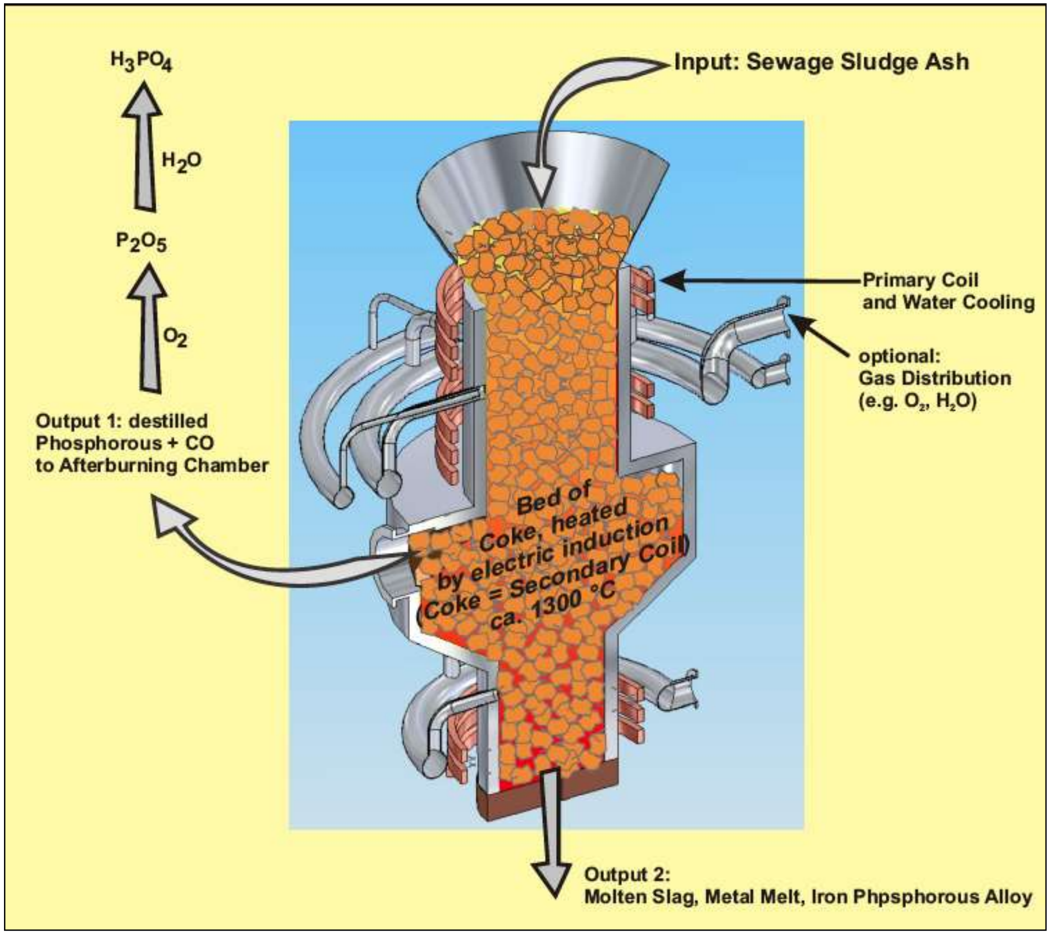


# Gas phase: e.g. RecoPhos model

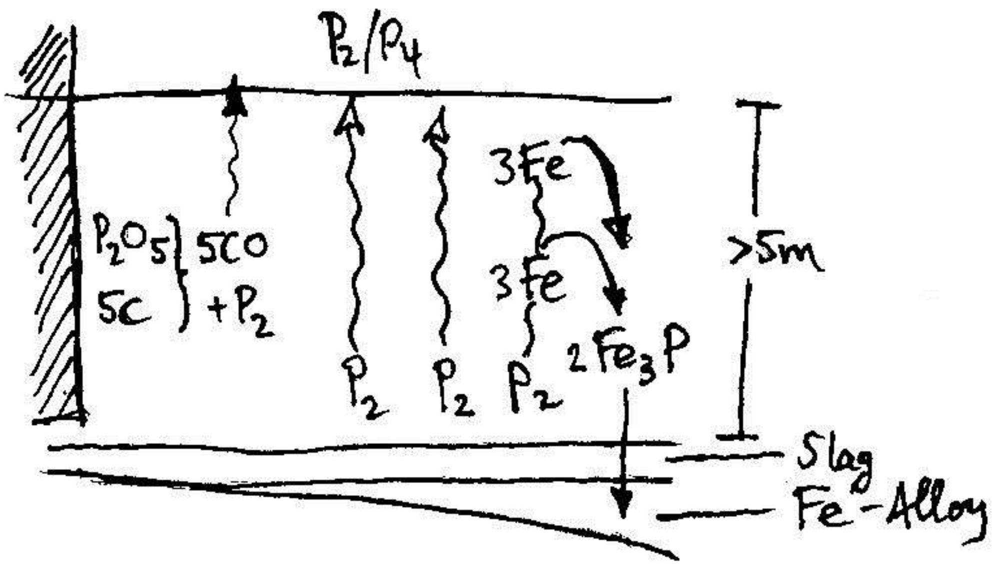
- Fuming reactor (reduction and evaporation of P)

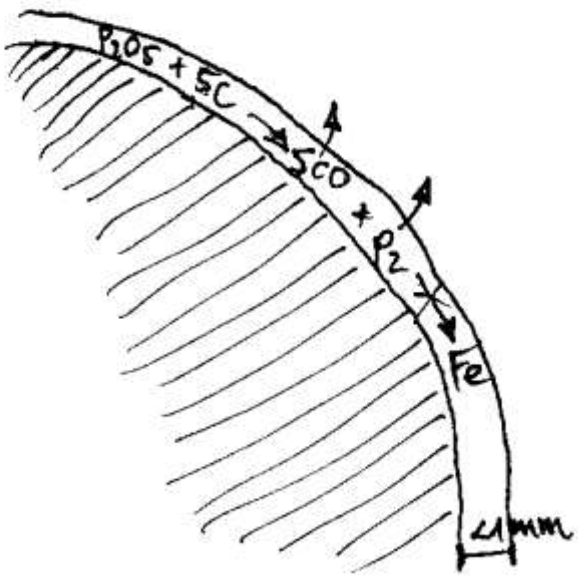



SCOPE newsletter/TPT website

# Questions in the RecoPhos process

- Will the thin-film reaction make a difference?
  - Reduction of P to gas phase before combination with Fe?




H. Raupenstrauch, ProcessNet

# Questions in the RecoPhos process

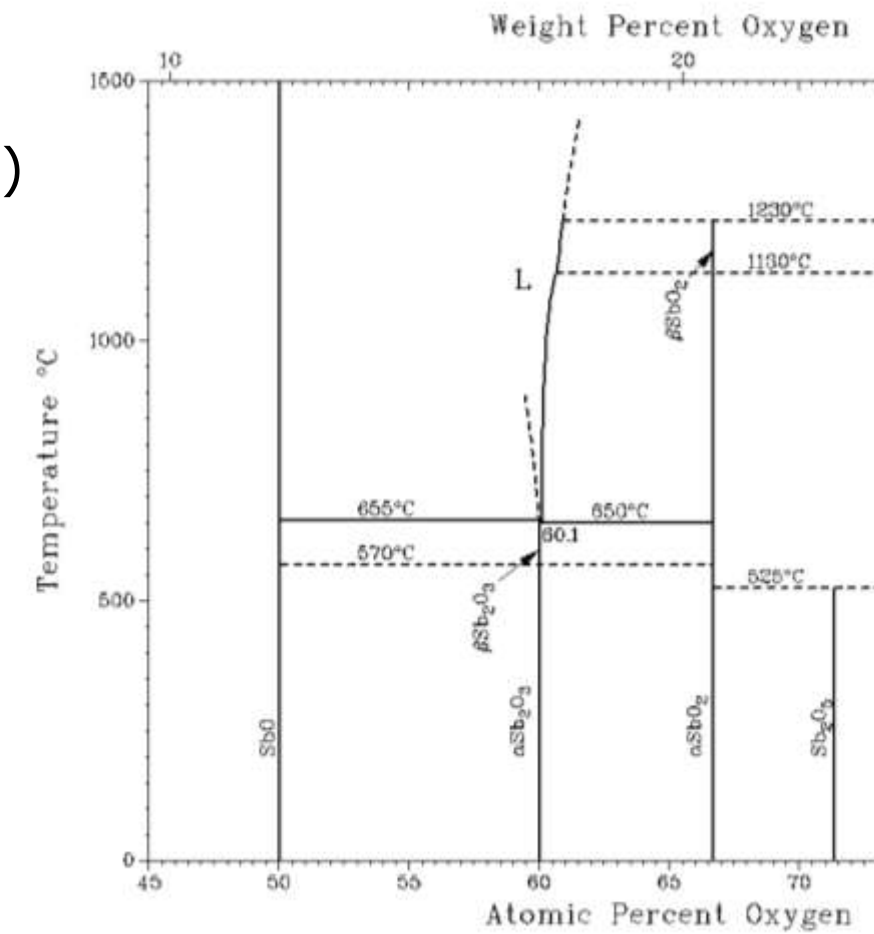
- How will the heavy metals behave?
  - Compounds in gas phase vs. activity in slag/metal
- Can we steer the slag:
  - Optimal viscosity
  - Lower/higher melting temperature
  - Higher P yield
  - Some phase diagram optimisation with $P_2O_5$

# Thermodynamics of the gas phase

- Also in other processes, lots of evaporation occurs
  - Of course $SO_2$, CO...
  - Also impurities As, Cd,...
  - And the main metal, certainly in case of Pb
  - Interaction to form volatile chlorides, oxides, sulphides...
    - E.g. vapour pressure of lead
  - On cooling, complex compounds
    - E.g. sulphates, arsenates, chlorides

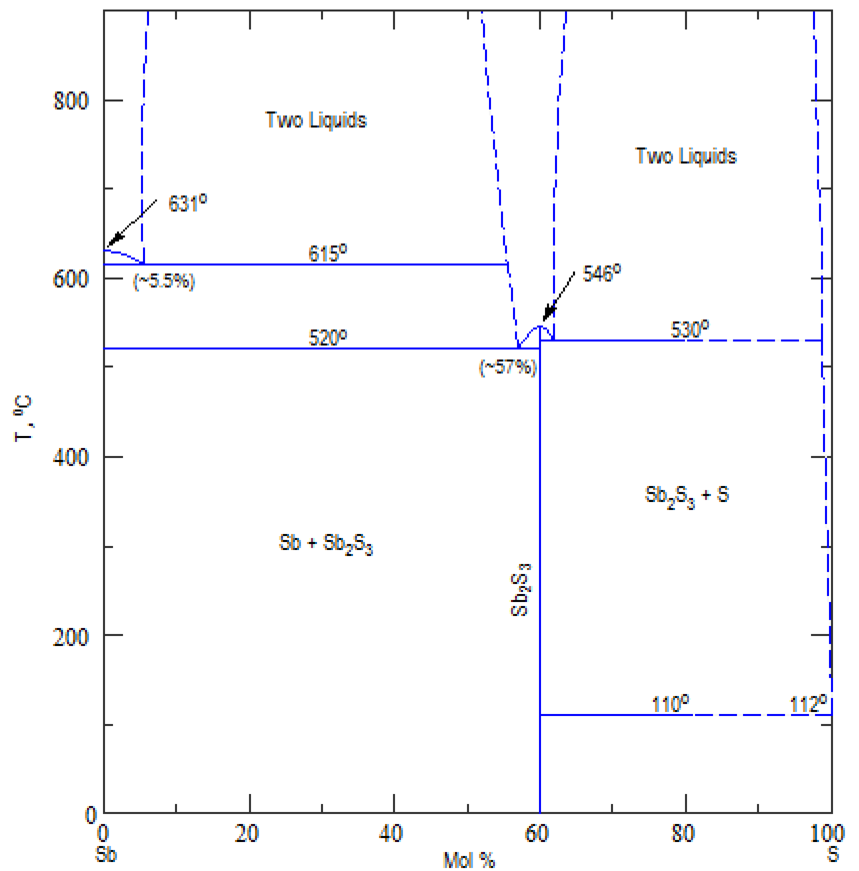
# The case of Sb

- $Sb_2O_3$, a stable oxide known to sublime as $Sb_4O_6$
- FactSage 6.2:
  - Melting at 656°C
  - Evaporation at 2467°C ($Sb+O_2$)
- FactSage 6.3/4:
  - Melting at 655°C
  - Dissociation at 748/763°C to $SbO(g)$ + $SbO_2(s)$
  - Full evaporation at 998°C ($SbO + O_2$)
- Wikipedia:
  - Melting at 650°C
  - Sublimation at 1425°C



# The curious case of Sb

- Stibnite, $Sb_2S_3$, a known stable sulphide mineral
  - FactSage 6.2:
    melting at 550°C,
    boiling at 1534 ($Sb_2$+$S_2$)
  - FactSage 6.3:
    melting at 550°C,
    sublimation at 556°C
    ($Sb_2S_4$+$Sb_4S_3$)
  - FactSage 6.4:
    sublimation at 103°C
    ($Sb_2S_3$)
  - Phase diagram: well...




Lazarev 1973, Urazov 1960

# Conclusions

- Modelling provide a framework for problem solving and fits well in a long term knowledge management strategy
- Apart from condensed phases, the gas phase is an integral part of a metallurgical process and need to be modelled with appropriate attention