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

dr. Sander Arnout, dr. Els Nagels
5 years InsPyro: references

**Lead**
- Recylex
- FMM
- Campine recycling
- Berzelius Metall
- BBH Stolberg
- STCM

**Zinc**
- ERAS
- Nyrstar
- Recytech

**Steel**
- Aperam
- Nedstaal
- Ascometal
- LSW

**Foundry**
- Magotteaux
- Allard
- Dovre

**Various**
- Sadaci
- Rio Tinto Minerals
- 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

Understanding the mechanisms of a process

Experience: knowledge how to run a process

Operating framework
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

- Equilibrium at constant $T$

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

### Charge Calculation for Lead Recycling (Simplified)

<table>
<thead>
<tr>
<th>Selection of raw materials</th>
<th>Amount (kg)</th>
<th>Water content (%)</th>
<th>Dry weight (kg)</th>
<th>Composition of dry fraction</th>
<th>Mass balance</th>
<th>Organics (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paste</td>
<td>1000</td>
<td>8.0%</td>
<td>920</td>
<td>Pb: 90.0% Fe: 0.6% Sb: 1.0% Ca: 0.5% Si: 1.0% Al: 0.5% Na: 3.0% S: 7.0% O: 0.5% C: 0.0%</td>
<td>828</td>
<td>0</td>
</tr>
<tr>
<td>Plates</td>
<td>1000</td>
<td>2.0%</td>
<td>980</td>
<td></td>
<td>956</td>
<td>0</td>
</tr>
<tr>
<td>Coke</td>
<td>25</td>
<td>2.5%</td>
<td>25</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Lime</td>
<td>5</td>
<td>5%</td>
<td>5</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Iron turnings</td>
<td>70</td>
<td>100.0%</td>
<td>70</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Soda ash</td>
<td>20</td>
<td>100.0%</td>
<td>20</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

#### Model estimation: using thermodynamic calculations

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Heat need/input</th>
<th>DEMO</th>
<th>kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Total weight (kg)

- **Bullion**: 1738 kg (Pb: 99.1%, Sb: 0.32%, O: 0.0%)
- **Slag**: 14 kg (CaO: 32.8%, SiO2: 37.4%, FeO: 3.9%, Na2O: 22.5%, PbO: 0.2%, Al2O3: 0.1%)

#### Matte

- **Total**: 159 kg (Fe: 40.7%, S: 16.2%, O: 7.3%, Na: 3.8%, Pb: 32.0%)

#### Gas

- **Total**: 100 kg (SO2: 0.04 kg)

#### Other phases

- **Total**: 8 kg (Fe excess: 0 kg, C excess: 0 kg)

#### Composition of raw materials

<table>
<thead>
<tr>
<th>Raw material name</th>
<th>Water fraction</th>
<th>Analysis dry fraction</th>
<th>Pb (%)</th>
<th>Fe (%)</th>
<th>Sb (%)</th>
<th>Ca (%)</th>
<th>Si (%)</th>
<th>Al (%)</th>
<th>Na (%)</th>
<th>S (%)</th>
<th>O (%)</th>
<th>C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plates</td>
<td>97.9%</td>
<td>99.0%</td>
<td>5.0%</td>
<td>0.0%</td>
<td>0.3%</td>
<td>3.0%</td>
<td>0.5%</td>
<td>0.5%</td>
<td>0.5%</td>
<td>0.5%</td>
<td>0.5%</td>
<td></td>
</tr>
<tr>
<td>Paste</td>
<td>98.0%</td>
<td>99.9%</td>
<td>5.0%</td>
<td>0.1%</td>
<td>0.5%</td>
<td>3.0%</td>
<td>0.3%</td>
<td>0.3%</td>
<td>0.3%</td>
<td>0.5%</td>
<td>0.5%</td>
<td></td>
</tr>
</tbody>
</table>

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**Inspiring metallurgy**

**Spark**
Stepwise simple process model

Equilibrium at constant T

Inspiring metallurgy
Process modelling – Pb recycling

- Effect of carbon on Pb recycling with CaO-FeO/Fe$_2$O$_3$-SiO$_2$ slag
- High Pb(l) at low reduction, but S-rich and PbS(g) losses

![Graph showing the amount of phase (kg) against the addition of C (g). The graph includes different phases represented by lines: g gas, g Pb-liquid, g Matte, g Slag, and g-C(s).](image-url)
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

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 accretion inevitable with the current mix, but linked to certain raw materials?
Accretion formation

Model explains evaporation and gas formation in the reactor

Model explains mechanism of dust formation (solids-liquids) upon cooling in the boiler

Model clarifies gas at this point (+ carry-over dust) = Link process to off-gas

Reactor: Unknown reaction
Scattered process conditions

Known input

Known output

Boiler

ESP: Known dust output
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)
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 $\text{P}_2\text{O}_5$
Also in other processes, lots of evaporation occurs

- Of course $\text{SO}_2$, 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$_2$O$_3$, a stable oxide known to sublime as Sb$_4$O$_6$**
- **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, \( \text{Sb}_2\text{S}_3 \), a known stable sulphide mineral
  - FactSage 6.2: melting at 550°C, boiling at 1534 °C (\( \text{Sb}_2+\text{S}_2 \))
  - FactSage 6.3: melting at 550°C, sublimation at 556°C (\( \text{Sb}_2\text{S}_4+\text{Sb}_4\text{S}_3 \))
  - FactSage 6.4: sublimation at 103°C (\( \text{Sb}_2\text{S}_3 \))
  - Phase diagram: well...

Lazarev 1973, Urazov 1960
Conclusions

- Modelling provides 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.