Modelling lead recycling processes

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GTT Annual Users' meeting 2013

InsPyro

InsPyro: inspiring metallurgy

- Consultancy company
- Based in Leuven, Belgium
- Customers DE, FR, NL, BE+
- Started 2009 and growing steadily

- Metallurgical process optimization and process development
- Software tools, course program

- Started with mainly steel, but quickly moved into non-ferrous
- Several references in lead recycling

Lead recycling

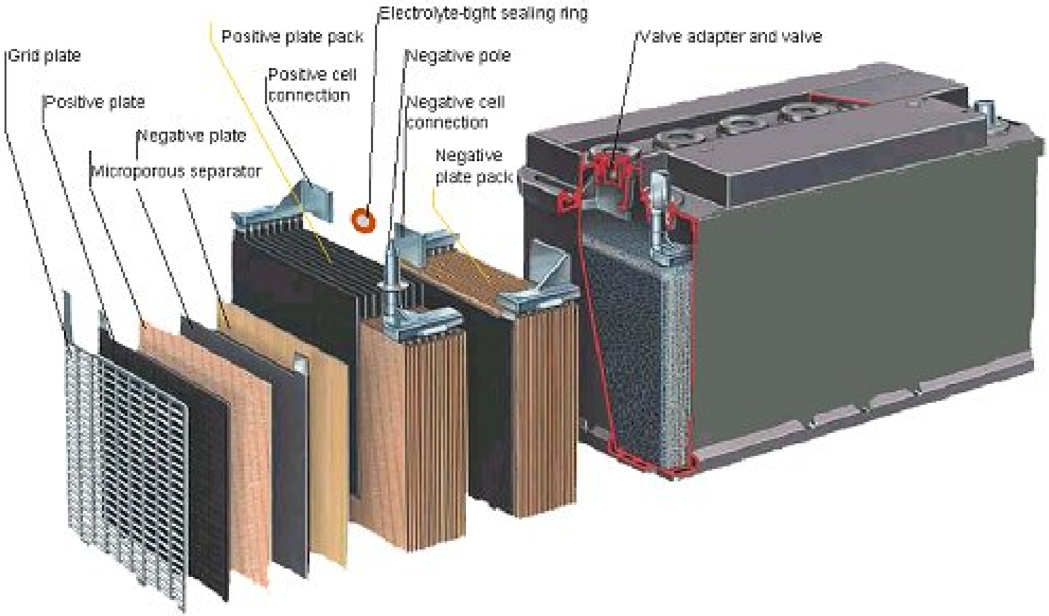
- Lead has a low melting point (330°C), high density (11 kg/dm³), and relatively low price (1500€/t)

- Lead used to be a component in several products, ranging from leaded petrol, paints, and tubes.
- Due to its toxicity, “distributed” applications are phasing out, but several “contained” applications remain where lead has unbeatable characteristics:
  - X-ray shielding
  - Anodes for metal production
  - Solders and semiconductors
  - Lead-acid batteries

- Contained applications guarantee appropriate recycling:
  - 99% recycling of lead in Western world
  - Worldwide more recycled lead than primary lead produced

Lead recycling

- In volume, leads major application is lead-acid batteries, which are therefore also the main source for recycling



- Reactions on discharging:
  - $PbO_2 + HSO_4^- + 3H^+ + e^- => PbSO_4 + 2\ H_2O$
  - $Pb + HSO_4^- => PbSO_4 + H^+ + 2\ e^-$
- A major impurity in batteries is sulphur, from reacted plates and paste and from retained acid

Lead recycling

- A major impurity in batteries is sulphur, from paste and acid
- Smelting happens in relatively small scale, which does not allow for a sulphuric acid plant
- Sulphur needs to be captured either by paste desulphurization or during smelting
- Efficient additions during smelting are iron and sodium carbonate
- Pb reduction is relatively easy, but more reducing conditions are needed for good S capture

Process 1: Rotary furnace

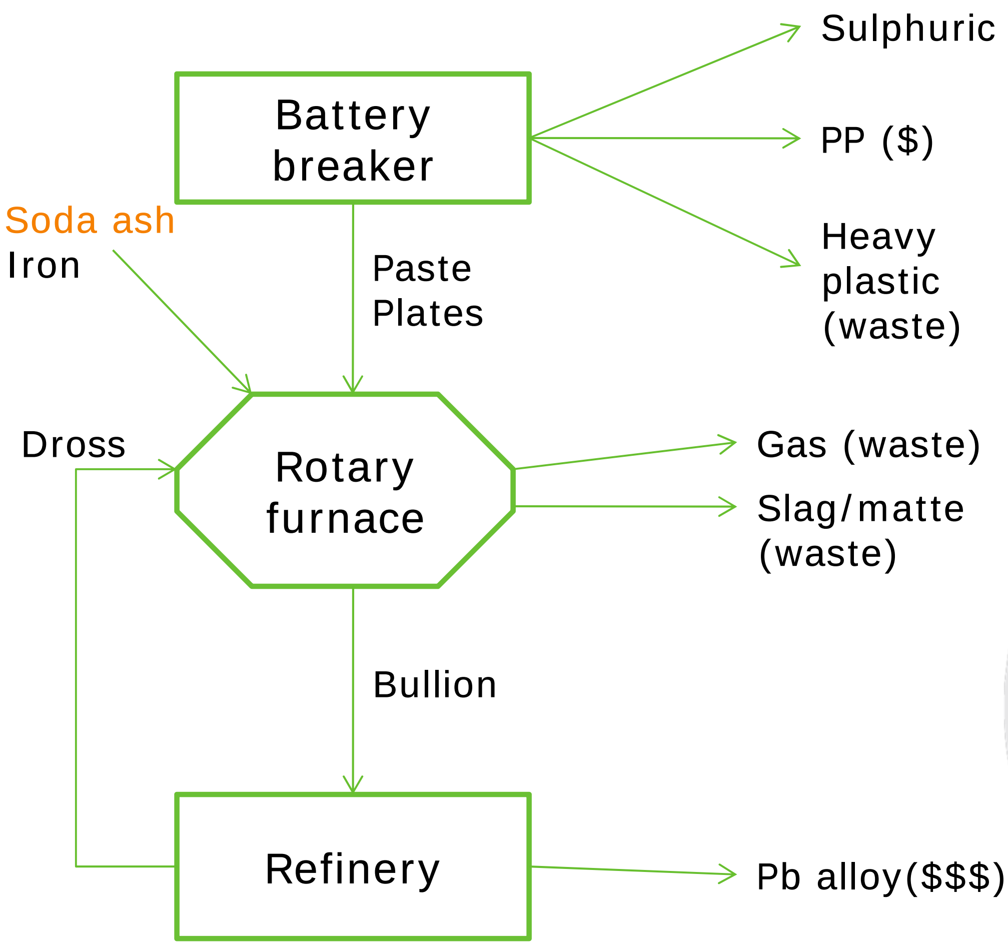
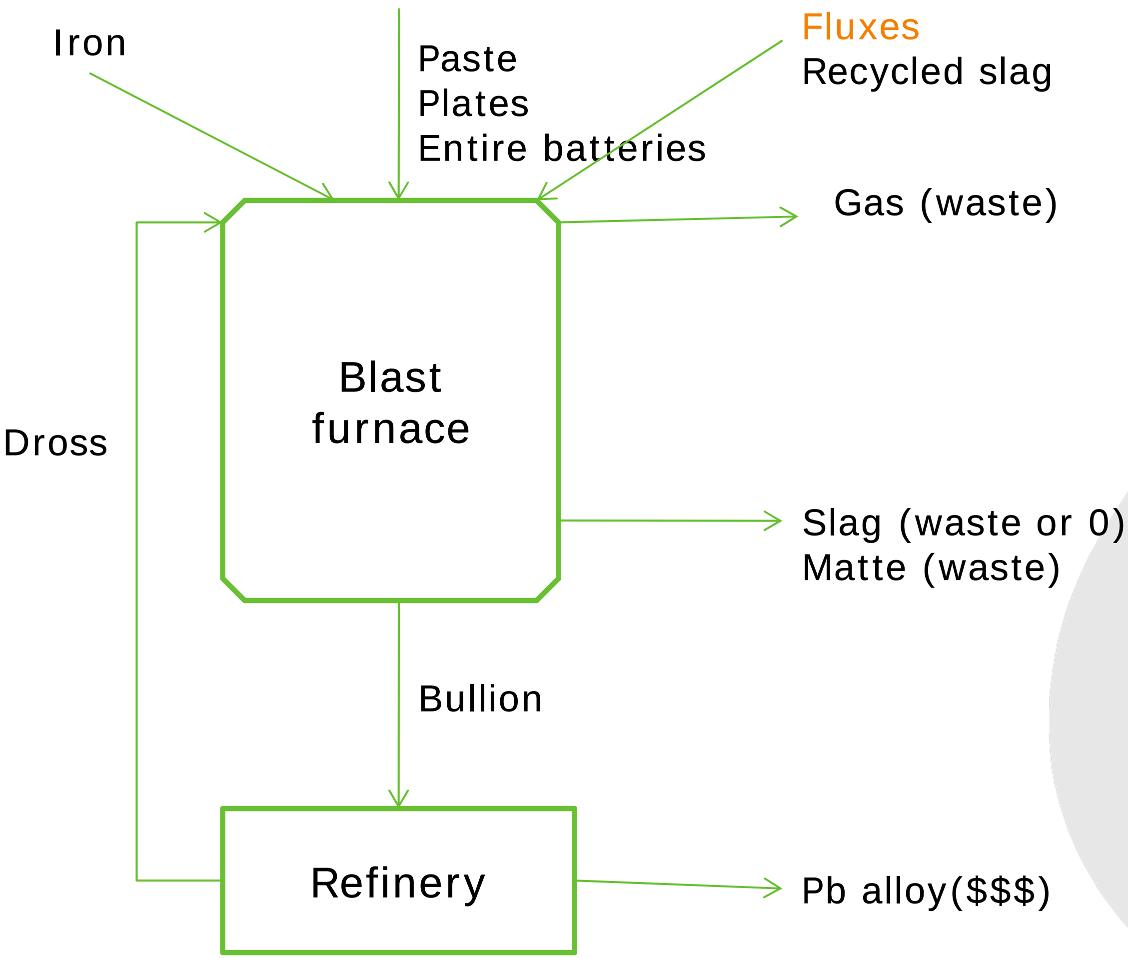
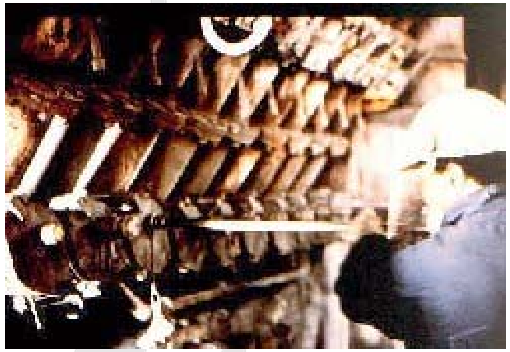
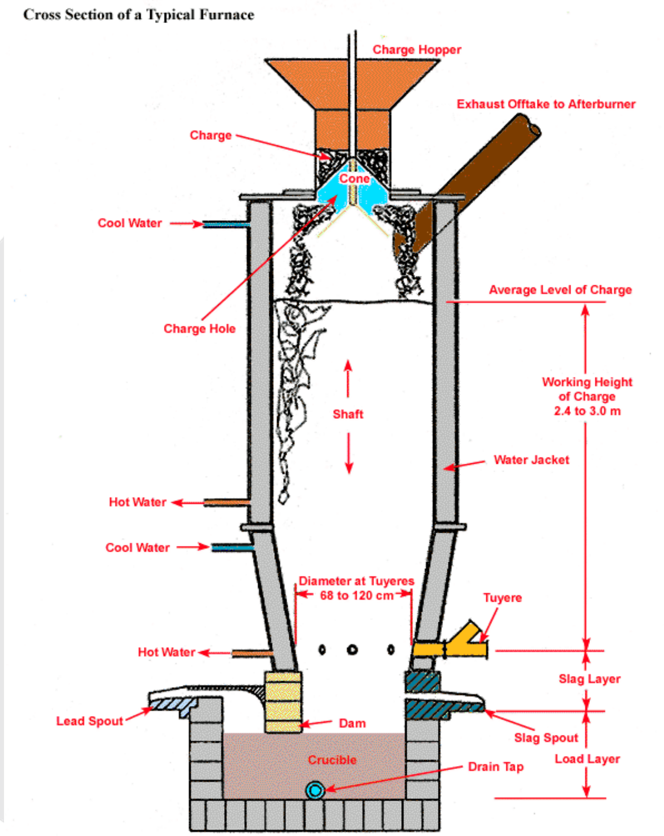


Photo: Recycle Eko-Start recycle.com.mk

Process 2: Lead shaft furnace



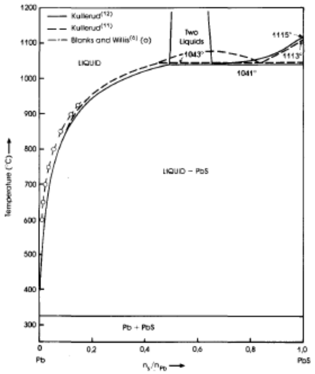


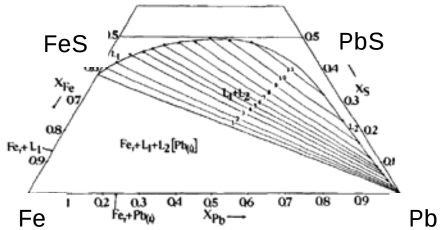


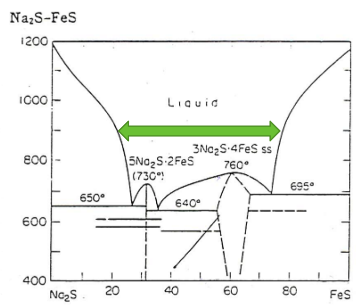
Pictures: US OSHA agency

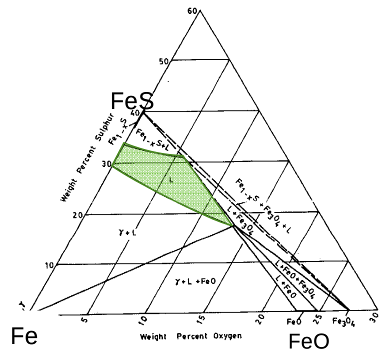
Thermodynamics of the matte

- 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”
  - Several particularities



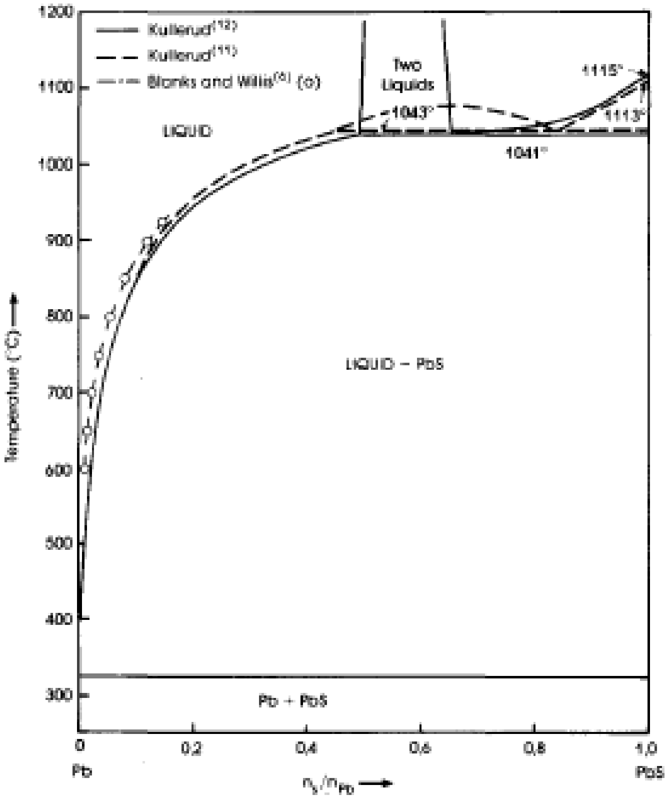


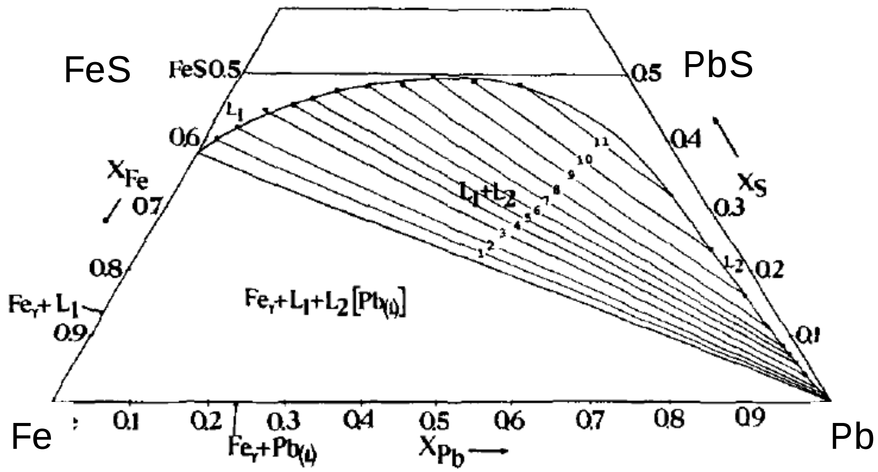




Thermodynamics of the matte

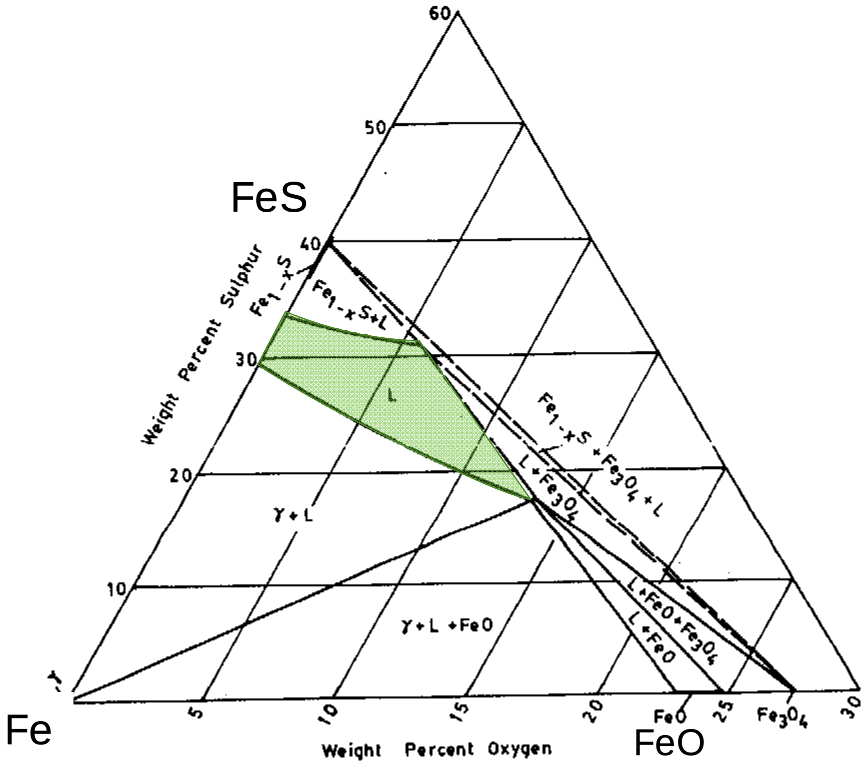
- High solubility for PbS in the matte phase
- But limited solubility for Pb when sufficient Fe present
  - Pb content not related to reduction of PbO but to S capture

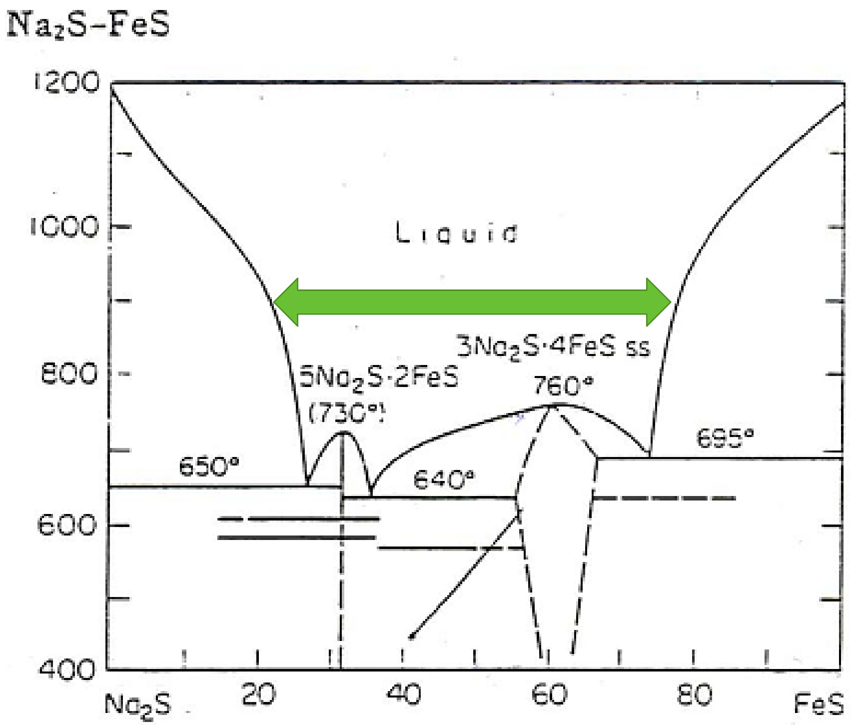




Thermodynamics of the matte

- Substantial solubility for FeO (not Fe_2O_3) and for Fe in "FeS (ℓ)"
- Lowering of melting temperatures with Na in system
- Sb behaviour very different from Pb

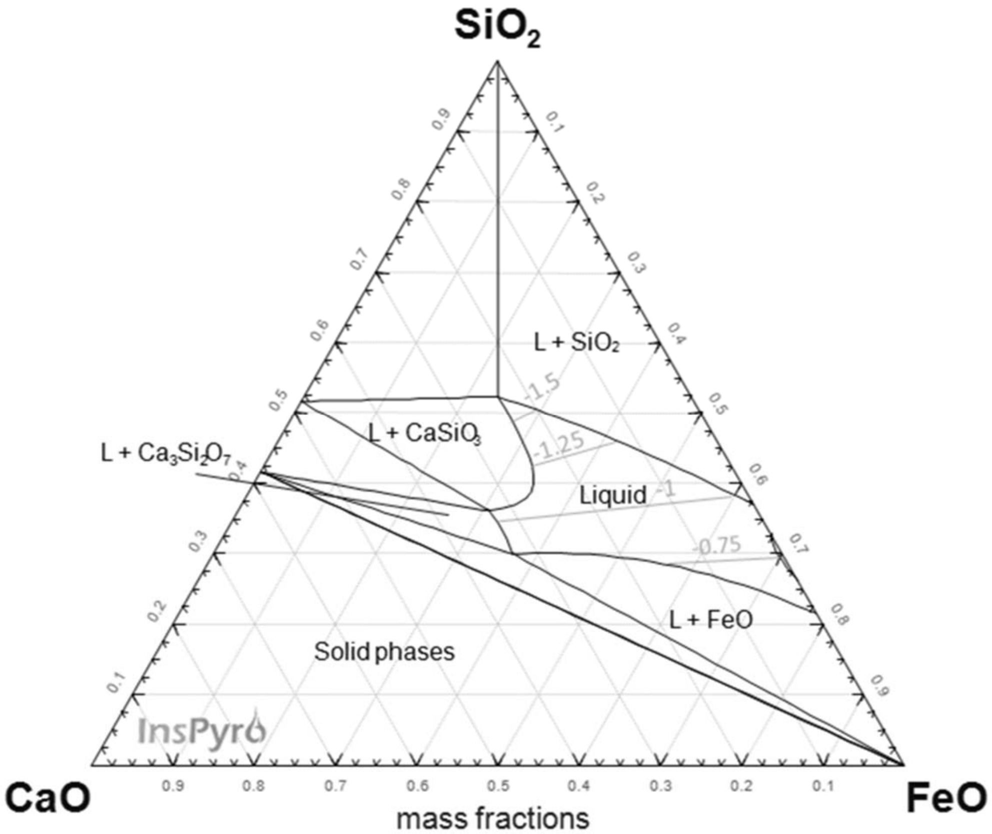


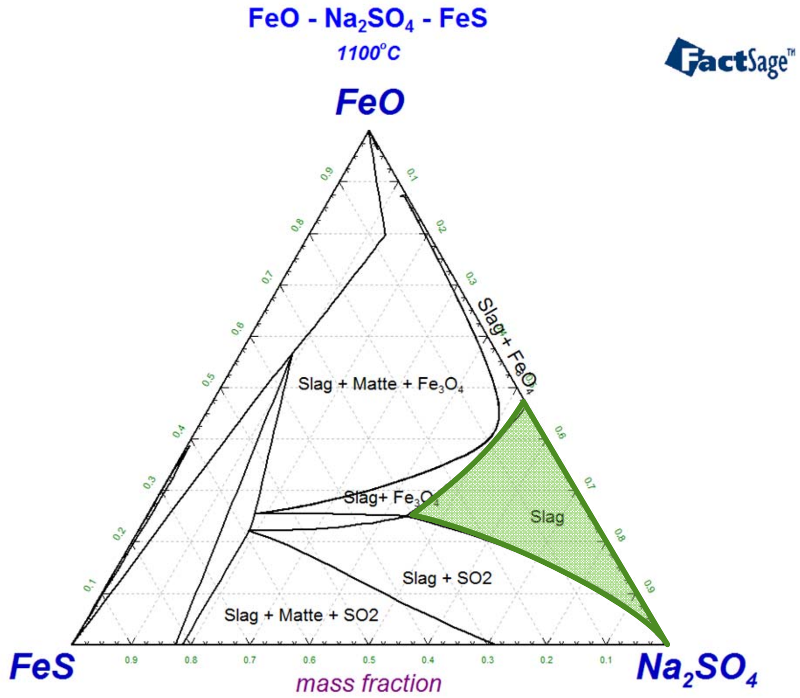


Thermodynamics of the slag system

- FeO-CaO-SiO_2-S system in fluxed Fe practice
- FeO-Na_2SO_4-PbO-S system in soda ash+Fe practice

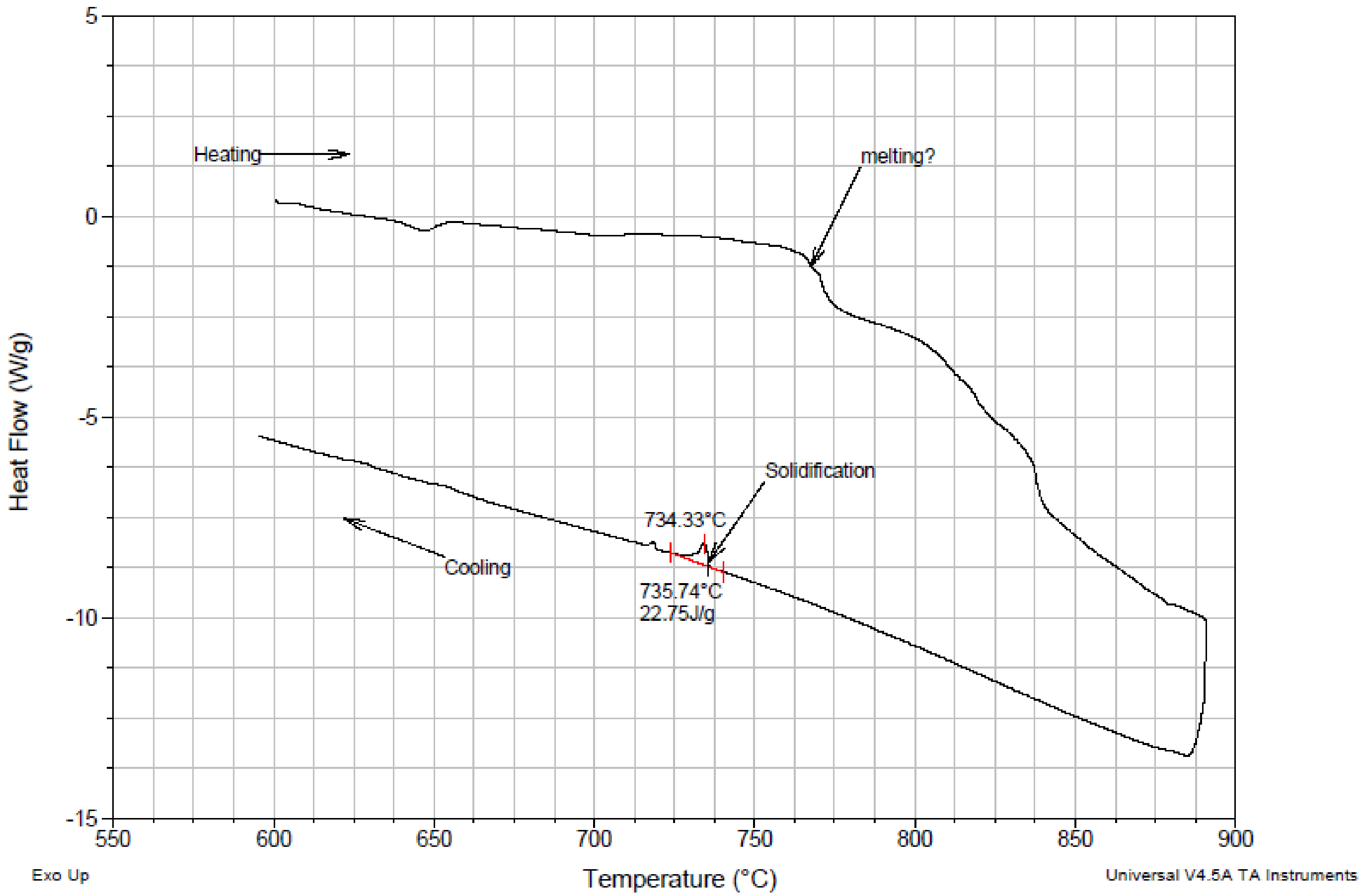
Salt oxide mixtures: very little data!





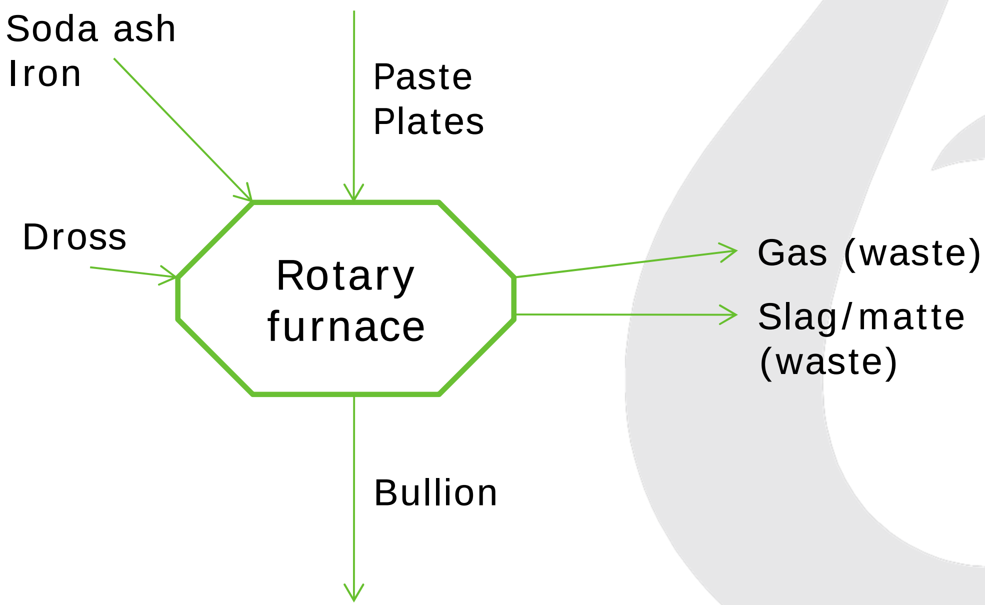
Rough estimation

DSC measurements on matte



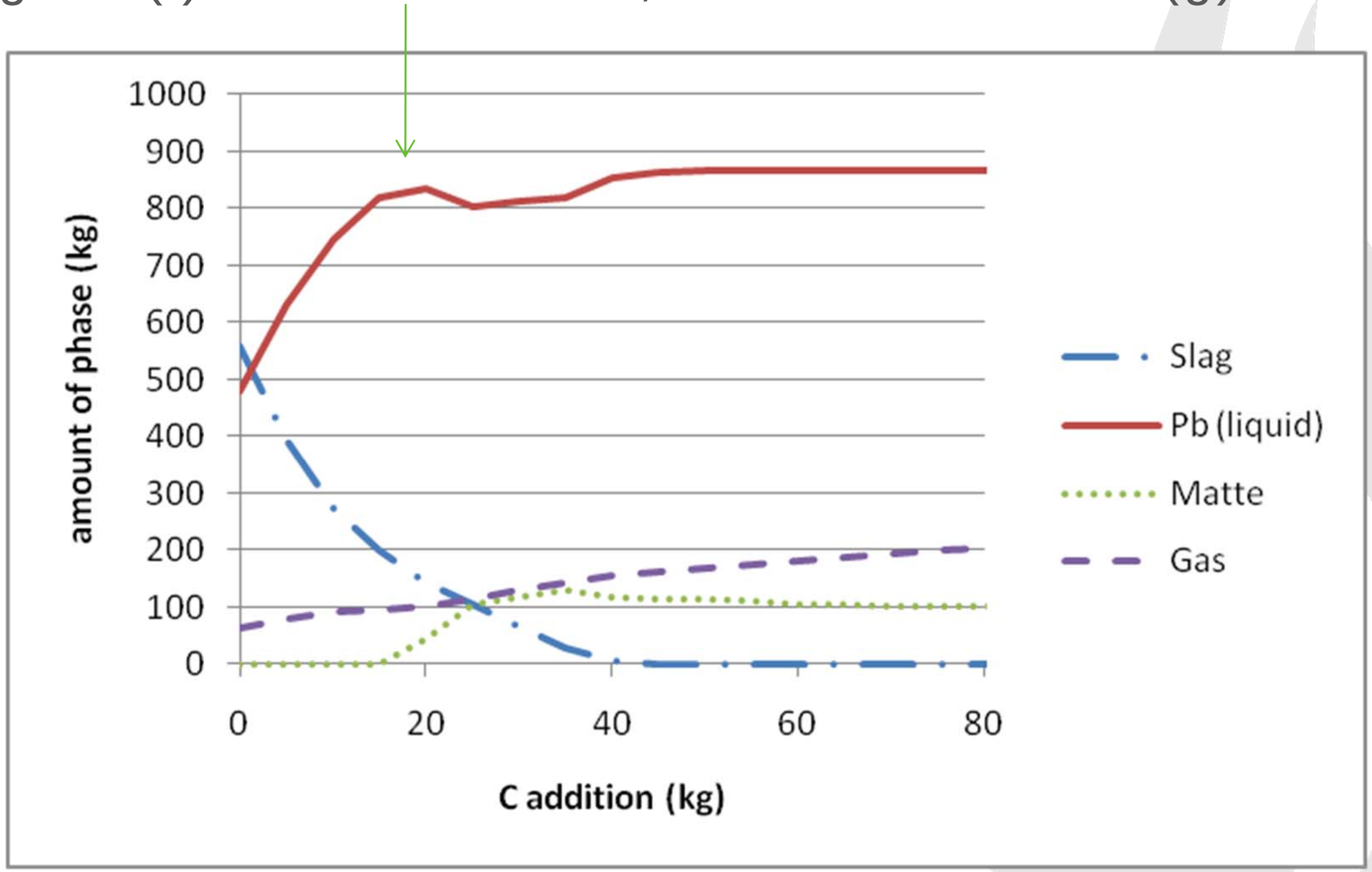
Modelling of the process

- Equilibrium calculations for rotary furnace (process 1)
  - Battery paste, metal, iron and sodium carbonate in charge
  - Temperature set to 950°C
  - Closed box equilibrium



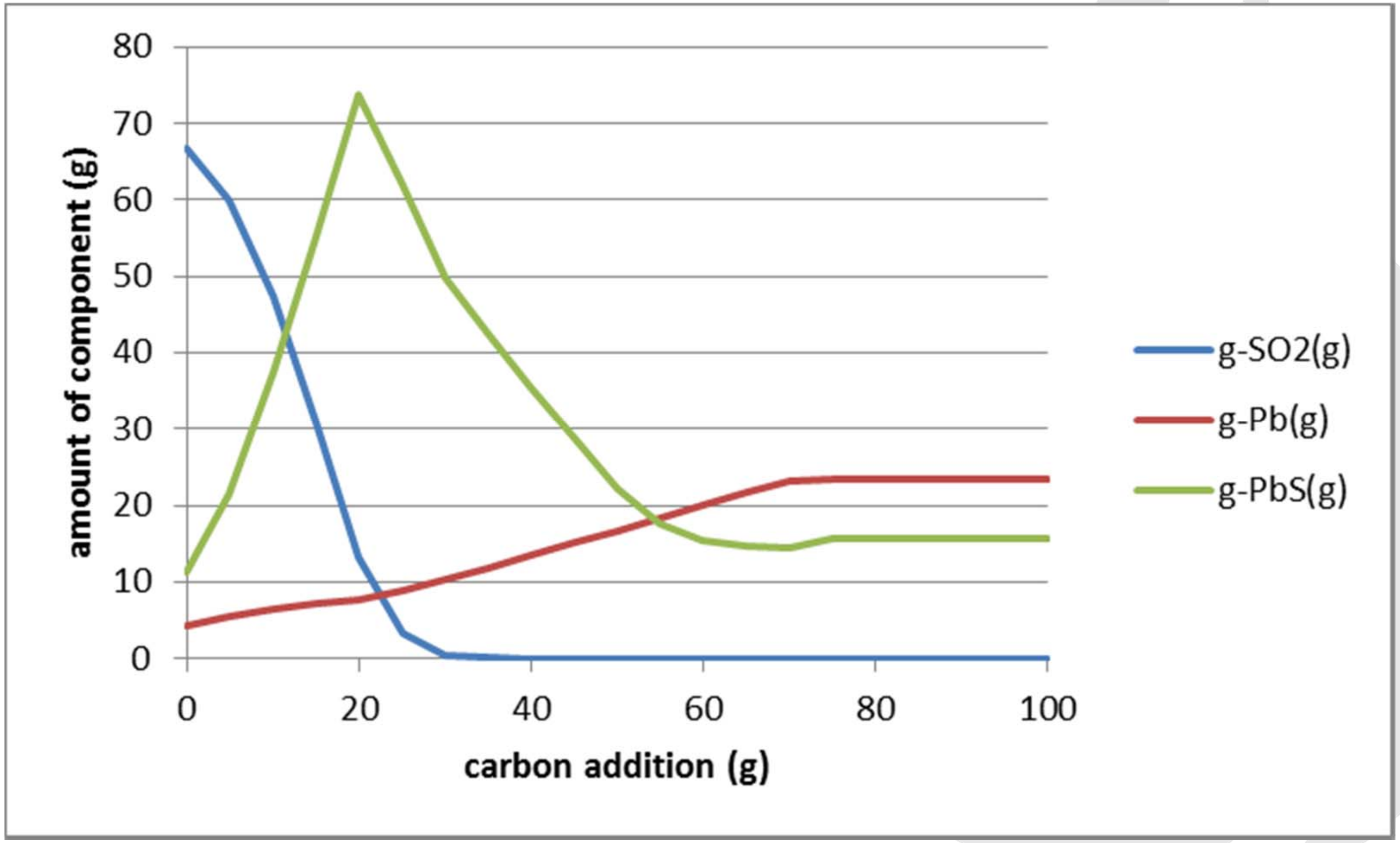
Process modelling - main phases

- Effect of carbon on system with CFS slag
- High Pb(l) at low reduction, but S-rich and PbS(g) losses



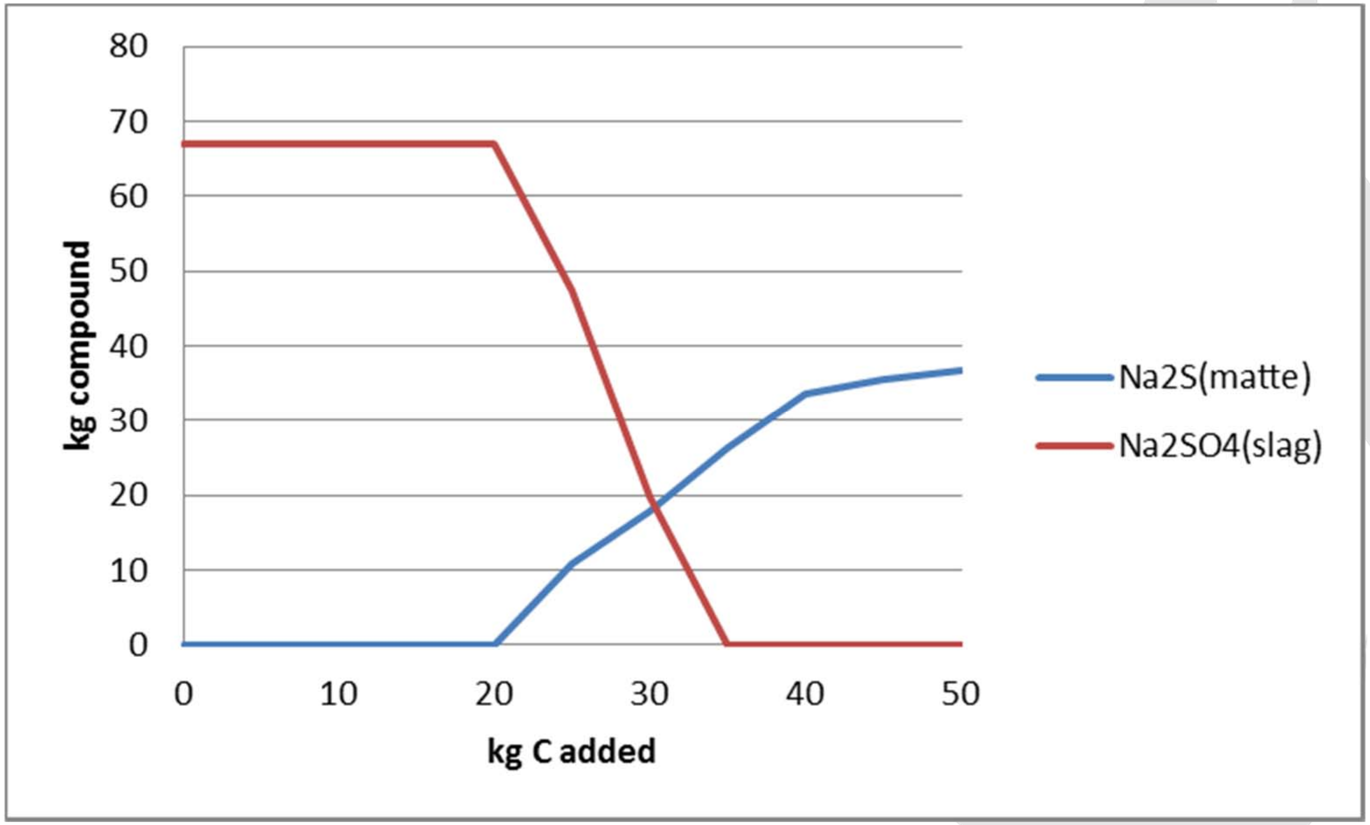
Process modelling - gases

- With formed CO, Pb and PbS evaporate
- SO_2 capturing only works well with sufficient reductants



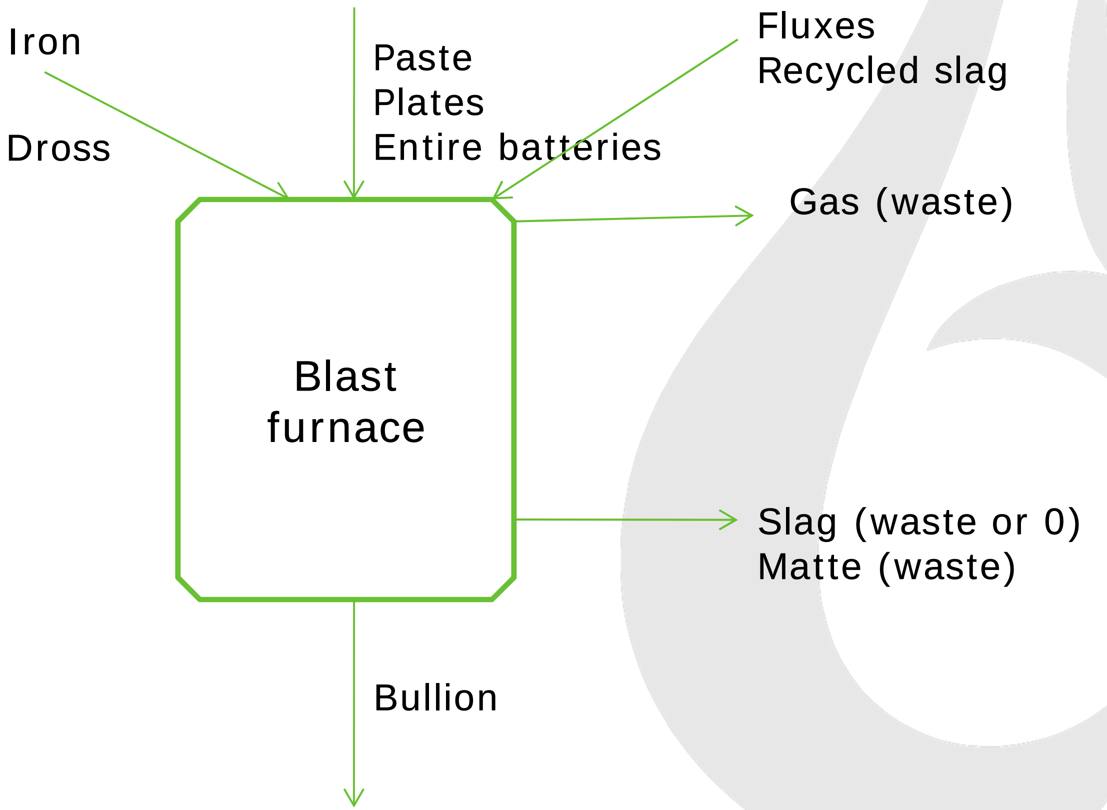
Process modelling – effect of Na_2CO_3

- Sodium state changes from Na_2SO_4 to Na_2S with reduction
- No large difference in amount of S => depends on iron



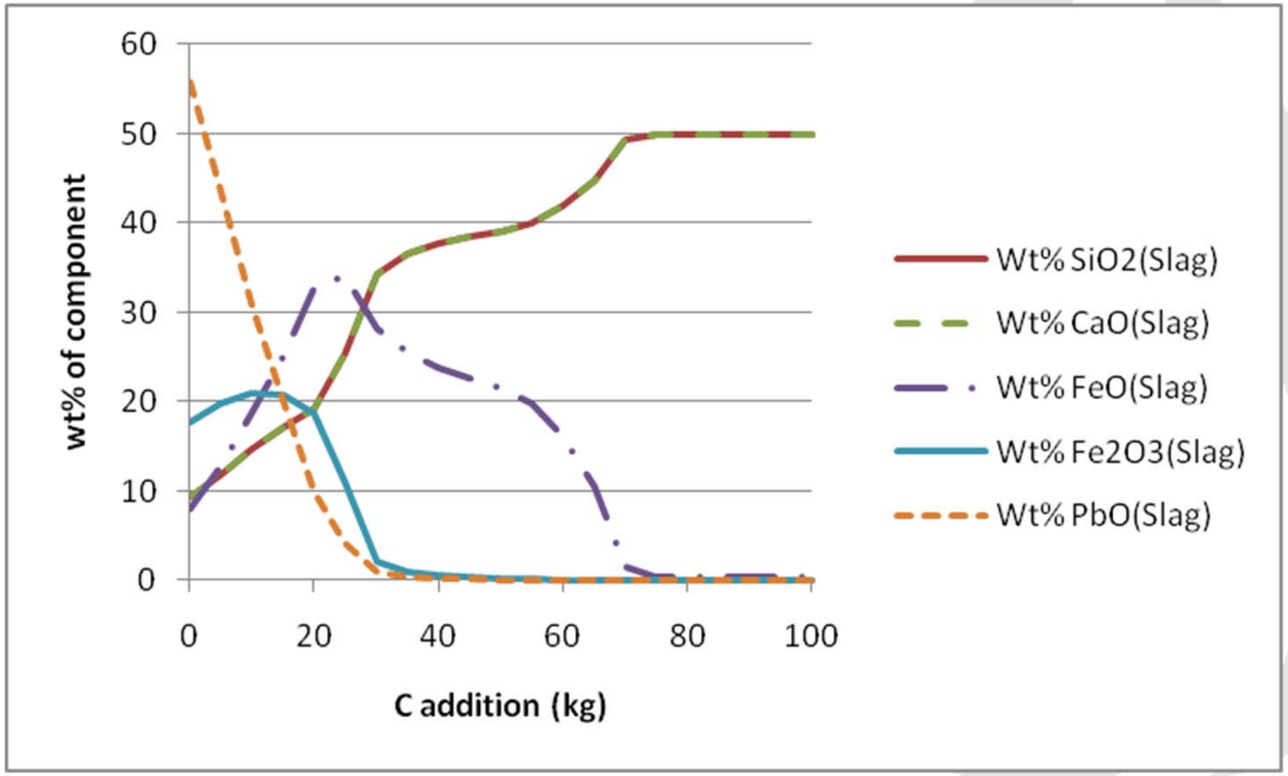
Process modelling – shaft furnace (process 2)

- Similar calculation, with recycled slag, no soda, at 1200°C



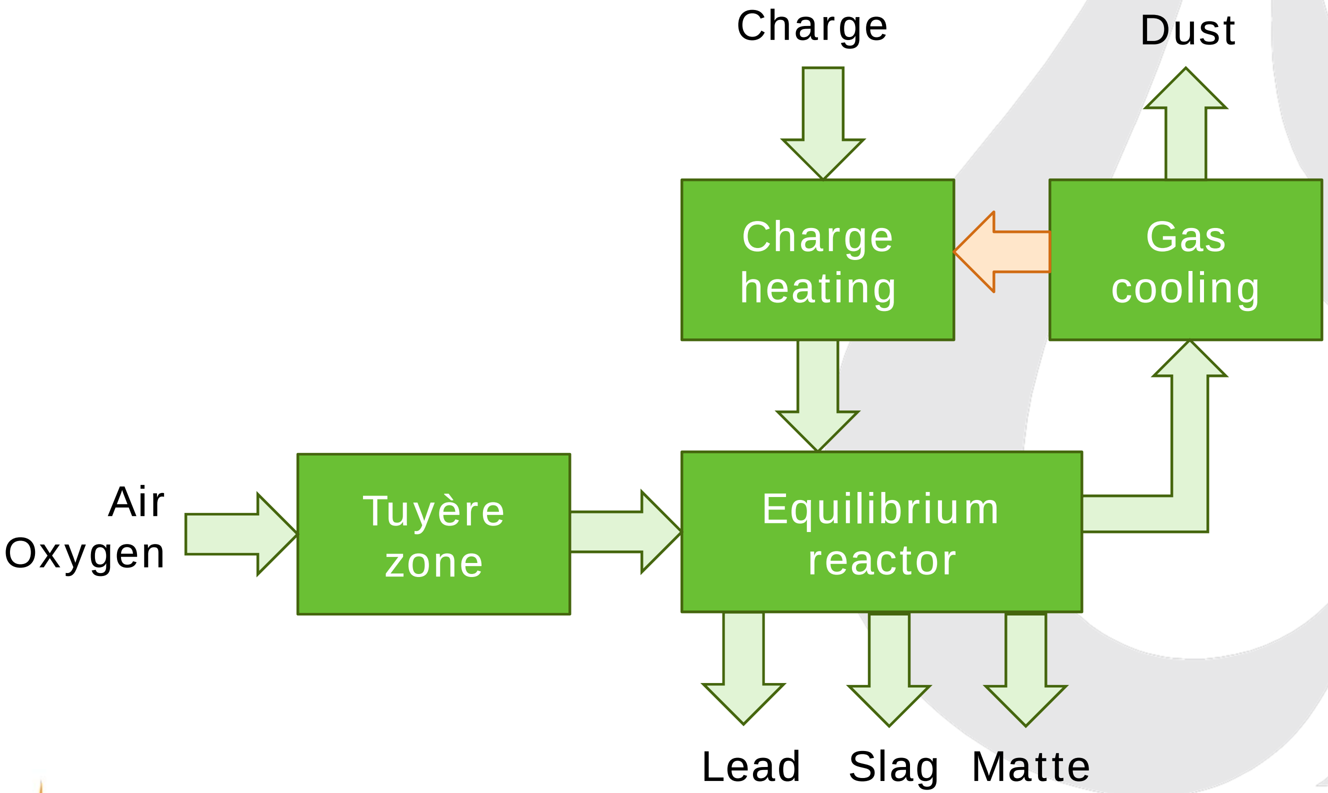
Process modelling – slag composition

- Effect of carbon on $CaO\text{-}FeO\text{-}SiO_2$ slag
- FeO as indicator of reduction: is not to be trusted
- FeO as indicator of amount of Fe: even worse!



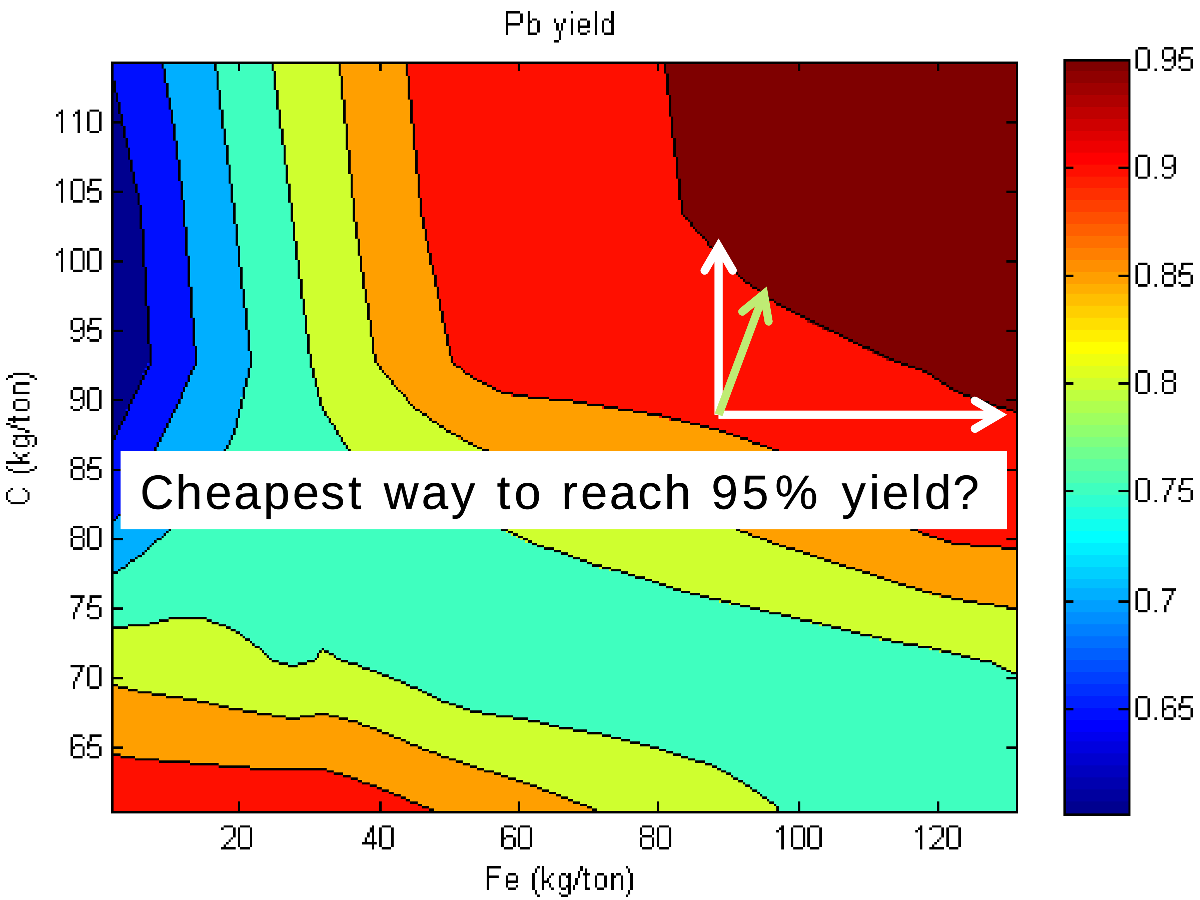
More detailed modelling of the process

- Simusage model for process 2
  - Easy to construct more complex model
  - Key is still in mass balance reconciliation and thermodynamic description



Process modelling

- Lead yield as a function of additions allows for economic evaluation



Process modelling

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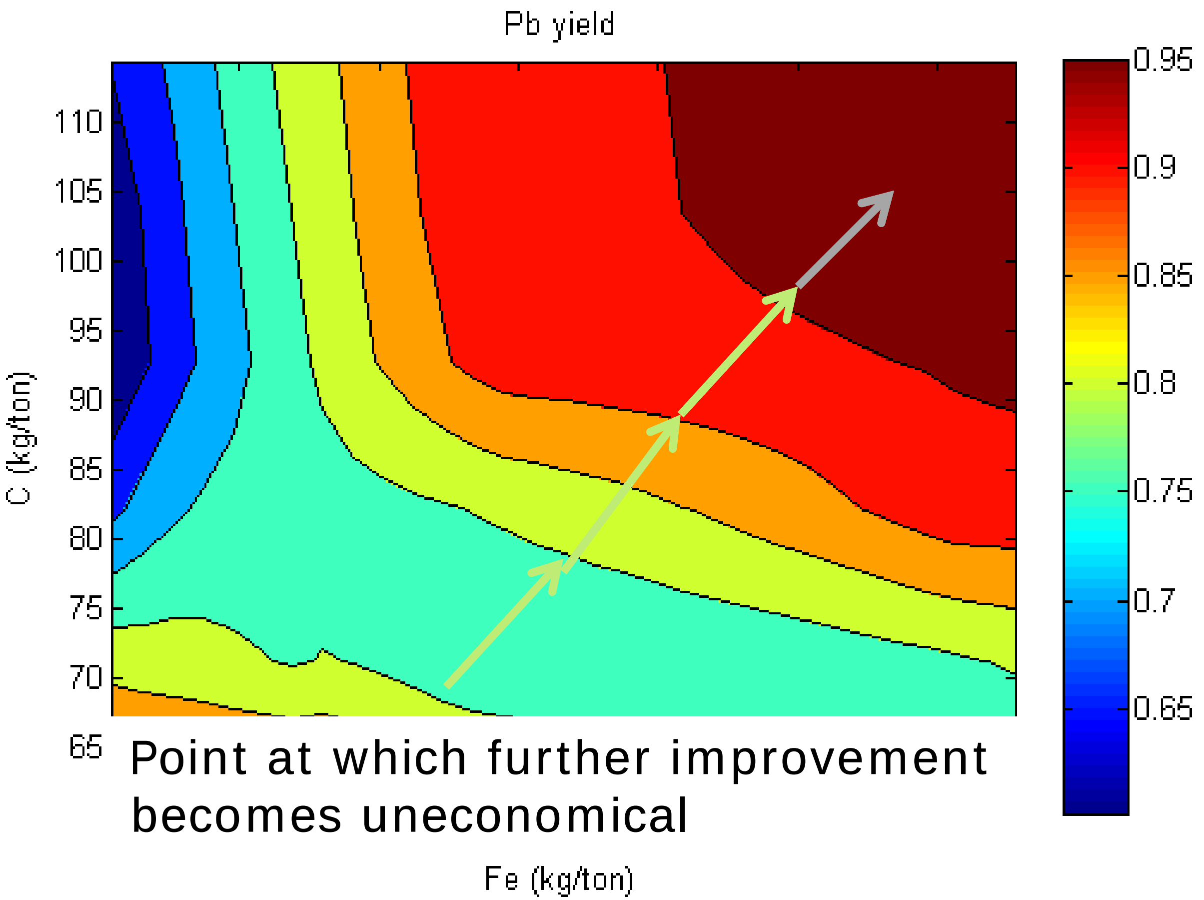

Conclusions

- In the work of InsPyro process modelling plays a key role
- Descriptive models help to understand process mechanisms and tendencies
- These can be a guide for process optimization
- Good thermodynamic descriptions remain crucial, as well as determining missing data in the lab…
- Realizing a predictive model is never easy, but if succesful, it can be used for faster process optimization and economic trade-offs