Modelling lead recycling processes

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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:
  - \( \text{PbO}_2 + \text{HSO}_4^- + 3\text{H}^+ + \text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O} \)
  - \( \text{Pb} + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + \text{H}^+ + 2\text{e}^- \)

- 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

Battery breaker
- Soda ash
  - Iron
- Paste Plates
- Dross
- Bullion

Rotary furnace
- Sulphuric acid (0)
- PP ($)
- Heavy plastic (waste)
- Gas (waste)
- Slag/matte (waste)

Refinery
- Pb alloy($$$)
Process 2: Lead shaft furnace

- **Paste Plates Entire batteries**
- **Fluxes Recycled slag**
- **Gas (waste)**
- **Slag (waste or 0) Matte (waste)**
- **Bullion**
- **Refinery**
- **Pb alloy($$$)**

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 Fe₂O₃) 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$_2$SO$_4$-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(I) 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 $\text{Na}_2\text{CO}_3$

- Sodium state changes from $\text{Na}_2\text{SO}_4$ to $\text{Na}_2\text{S}$ 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-FeO-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

![Diagram of the process](image)
Process modelling

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

Cheapest way to reach 95% yield?
Process modelling

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

Point at which further improvement becomes uneconomical
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 successful, it can be used for faster process optimization and economic trade-offs