Hydrogen reduction of entrapped metal oxides from fayalitic copper slags

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Full paper available in proceedings of copper 2022

HARARE

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Special thanks to Florian Wegmann

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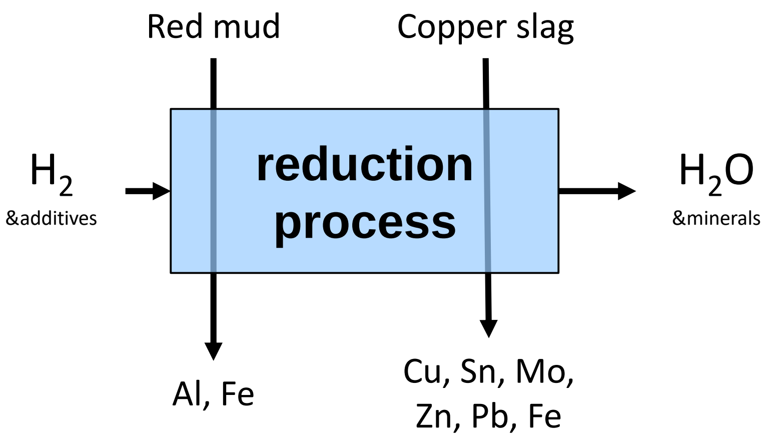
European project **HARARE**

- Demonstrate H_2-reduction for non-ferrous residues
- Laboratory to industrial scale
- Full process concept
  - Thermochemical simulation
  - Reduction processes
  - By-product evaluation and metal separation
  - LCA and economical study



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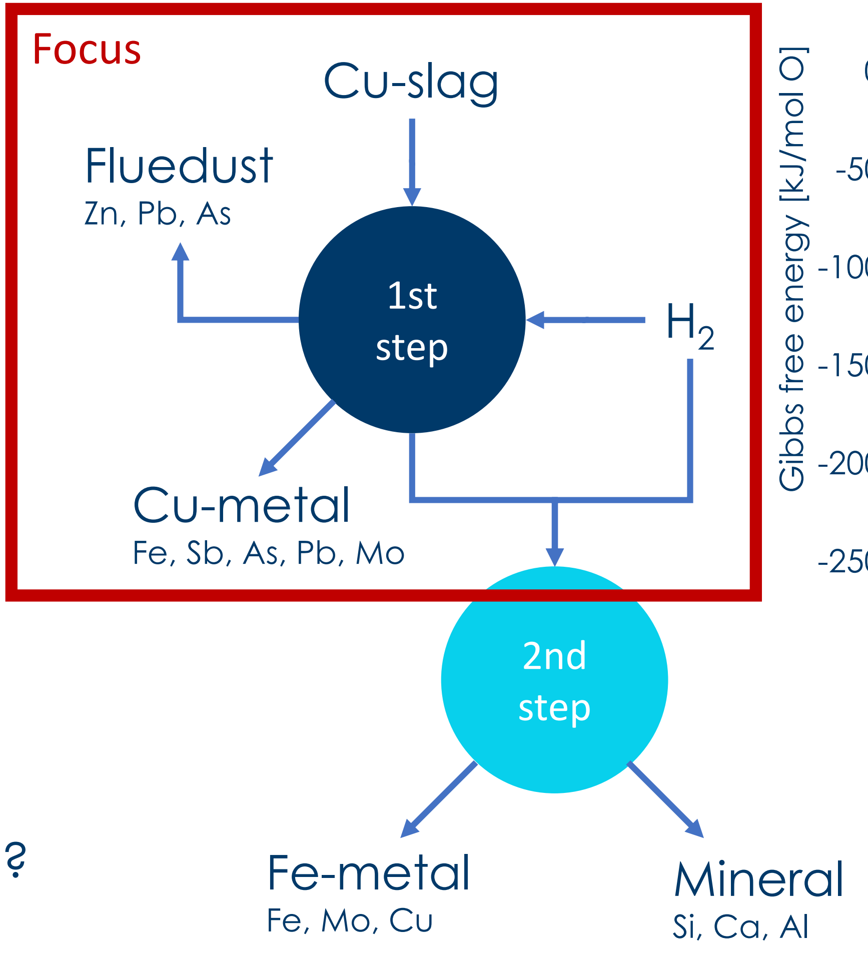
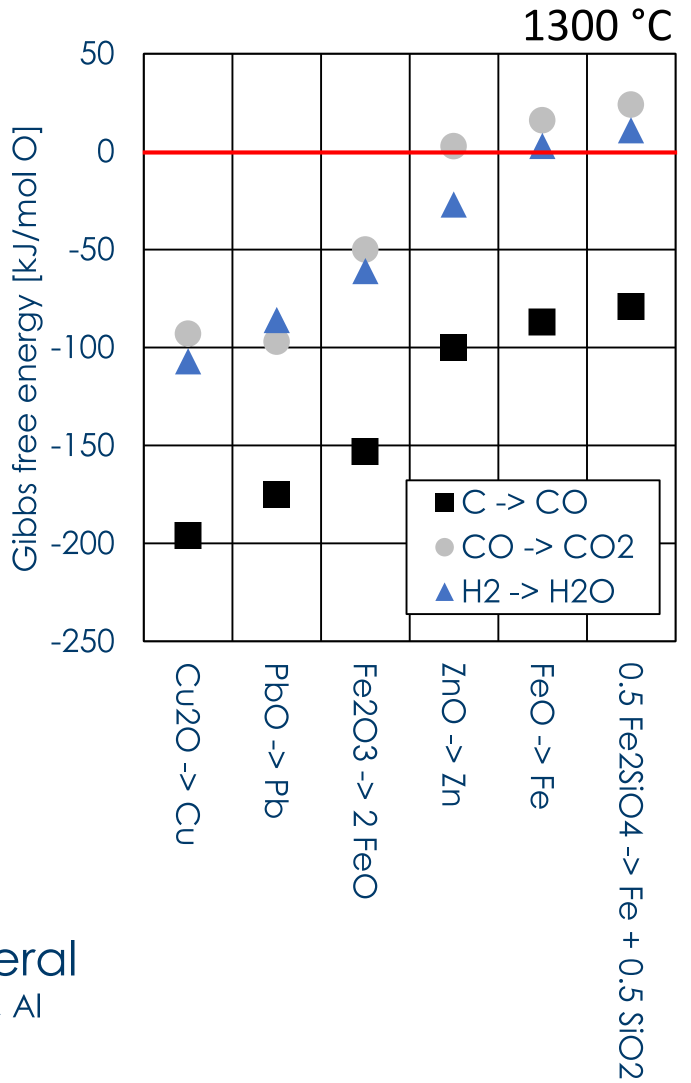
Flow sheet of process

- Selective copper reduction
  - Second step iron winning
- Focus on first step
  - **Selectivity**, **Efficiency**, Influence of H_2-conc., kinetics, …
- Why H_2 instead of C, CH_4 or CO?
  - Fast kinetics
  - High selectivity





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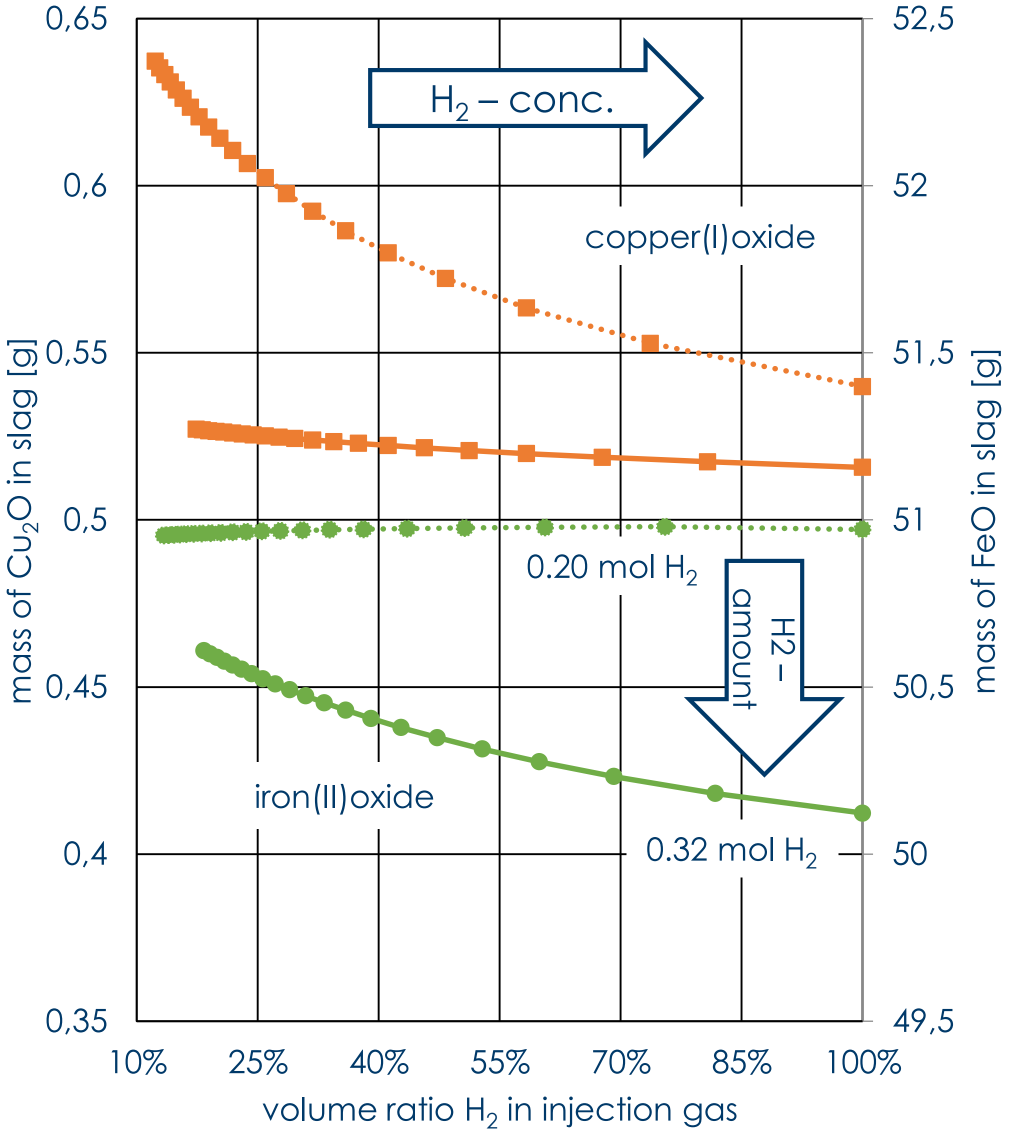
Thermochemical simulation (reduction)

- Higher concentration of reduction gas lowers Cu_2X content
- Barrier at around 0.52 wt.% Cu_2X
- Low hydrogen amounts don't reduce iron(II)oxide
- Hydrogen yield between 28.8 – 36.9 %
    - Lowers with an increase in H_2 concentration



Simulations done with FactSage™ 8.0

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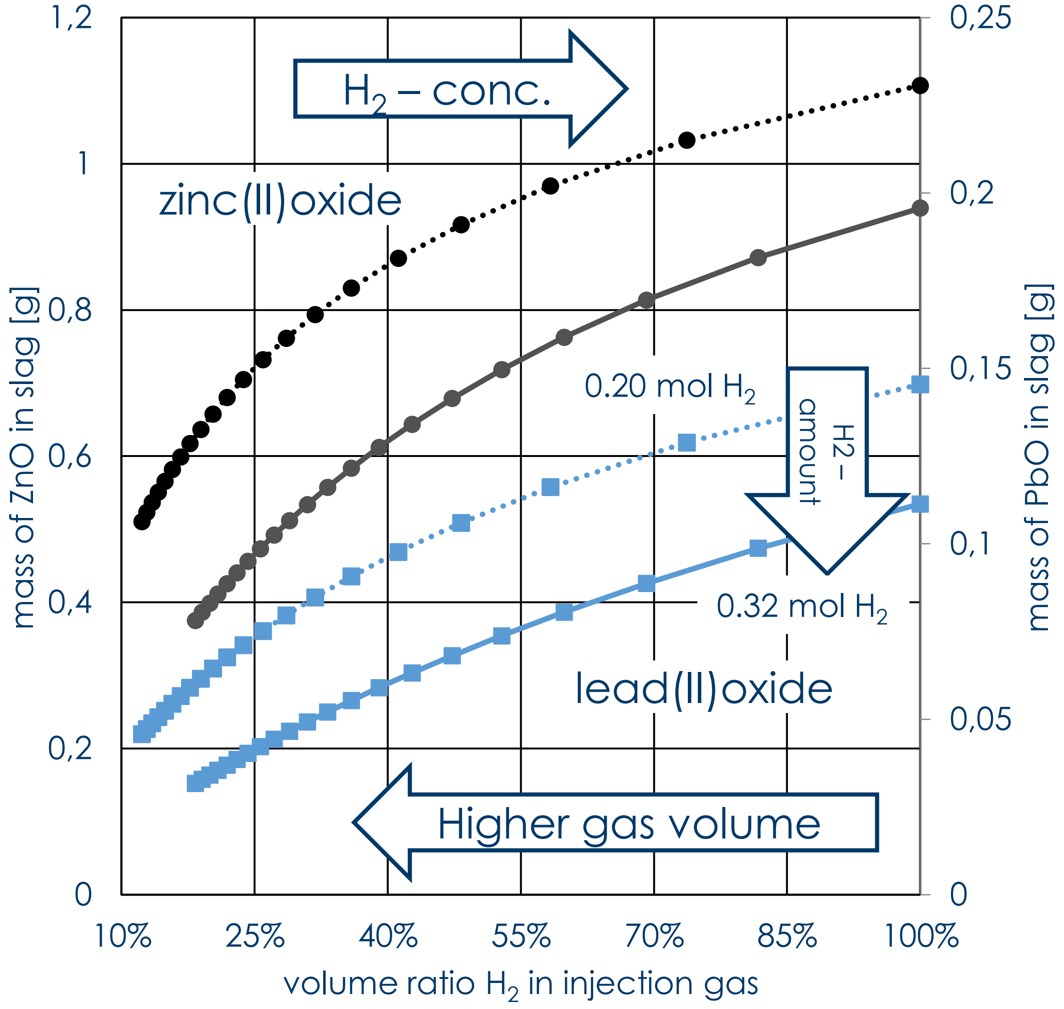
Thermochemical simulation (fuming)

- Fuming of slags possible
  - Achieving ∑(Zn+Pb) < 0.5 wt.% with 0.32 mol H_2/100 g slag
- Higher gas volume increases fuming effect
- Lowering Zinc and lead with low iron reduction

➢ Simulation confirms idea of selective reduction



$$vol.\%_{H2} = \frac{V_{H2}}{V_{H2} + V_{N2}}$$

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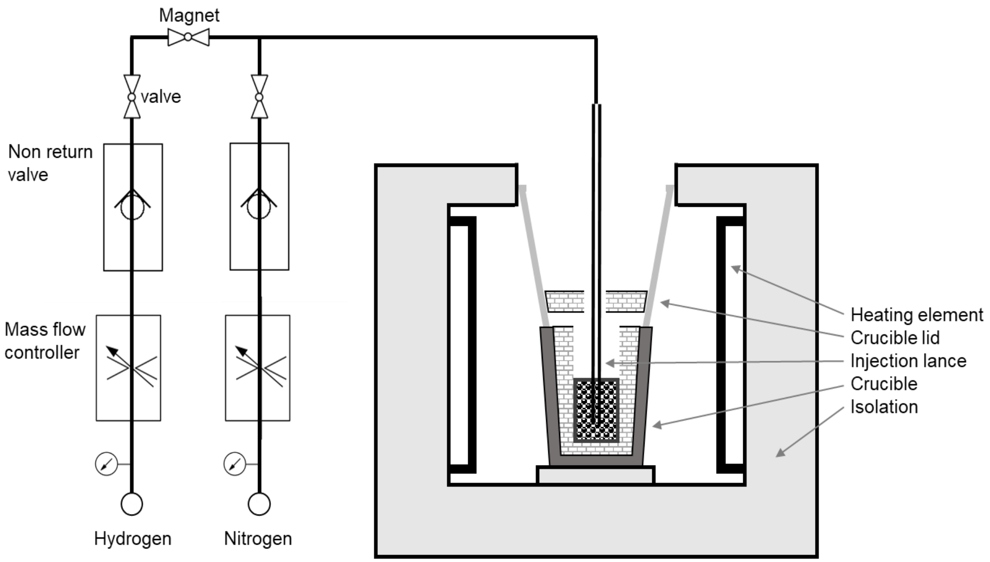
Setup and material

- Resistant heated furnace
- Gas mixing box with mass flow controllers
- Al_2O_3-Cr_2O_3-lining in crucible
- Al_2O_3 based lances
- Slag temperature ~1300 °C
- Two samples taken at ½ and full H_2 amount



Wt.%	FeO	SiO_2	Al_2O_3	CaO	Cu	Mo	PbO	ZnO	S	rest
Slag 1	50.1	31.8	4.5	2.2	1.4	0.6	0.3	1.3	0.4	5.4
Slag 2	50.1	33.9	4.1	2.2	1.3	0.3	0.2	0.7	0.3	4.7

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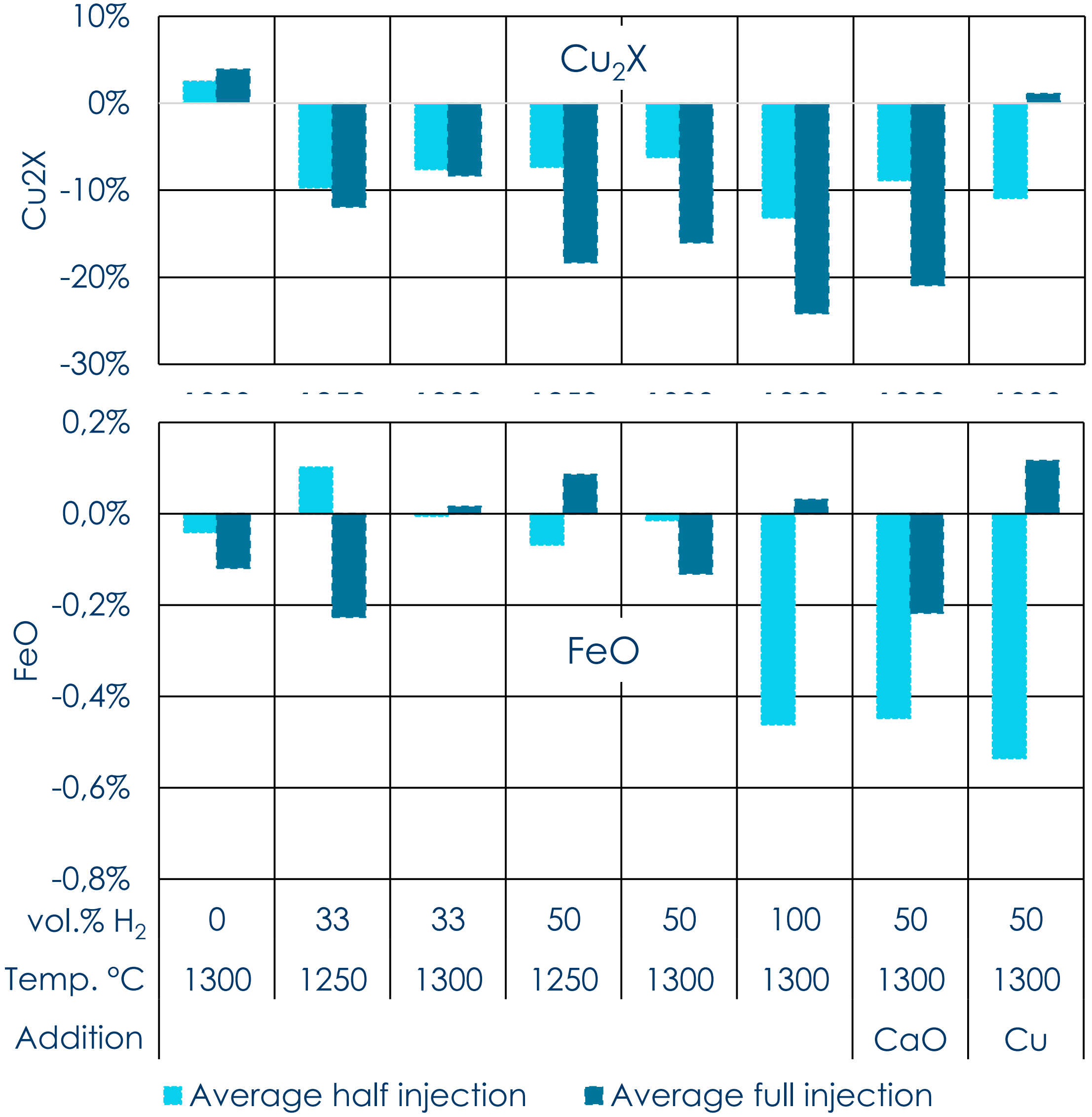
Experimental results (reduction)

- Higher H_2 concentration leads to higher Cu_2X reduction
  - (max 24.2 %, 1.09 wt.% - starting 1.52 wt.%)
- 100 % H_2 in reduction gas leads to iron reduction
- Lime increases the reduction yield of Cu_2X



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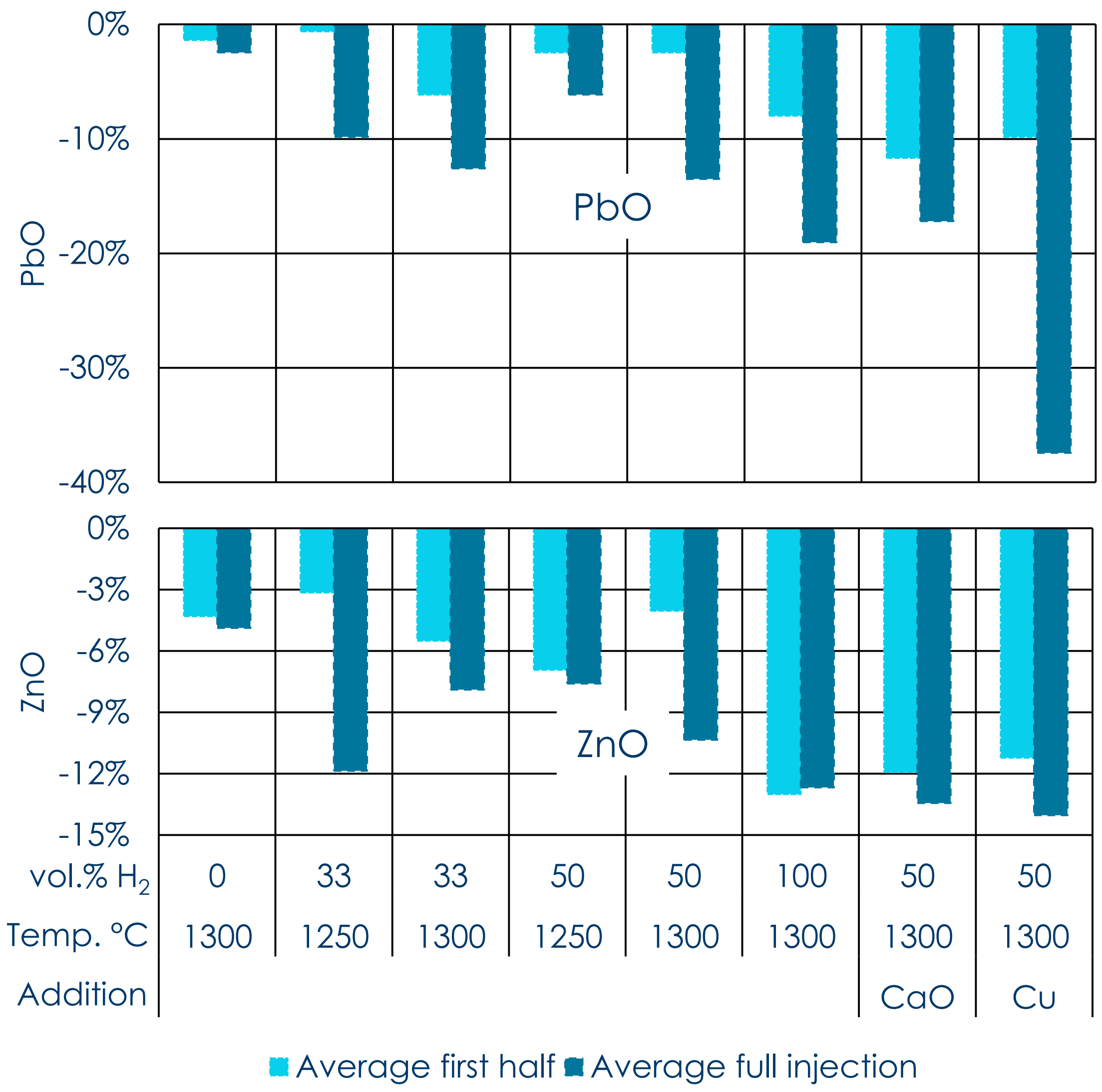
Experimental results (fuming)

- Lead reduction similar to copper
- Zinc fuming possible with various H_2-concentrations
- Influence of volume from simulation can not be confirmed
  - High fuming yield with high hydrogen concentration



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Efficiency of hydrogen reduction

- Efficiency of FactSage™: 29 - 37 %
  - ➢ Strongly depends on Cu-content
- Experimental efficiency: 10 – 17 %
  - ➢ 27 to 58 % of simulations in small scale
  - ❖ < 10 cm slag column for reaction

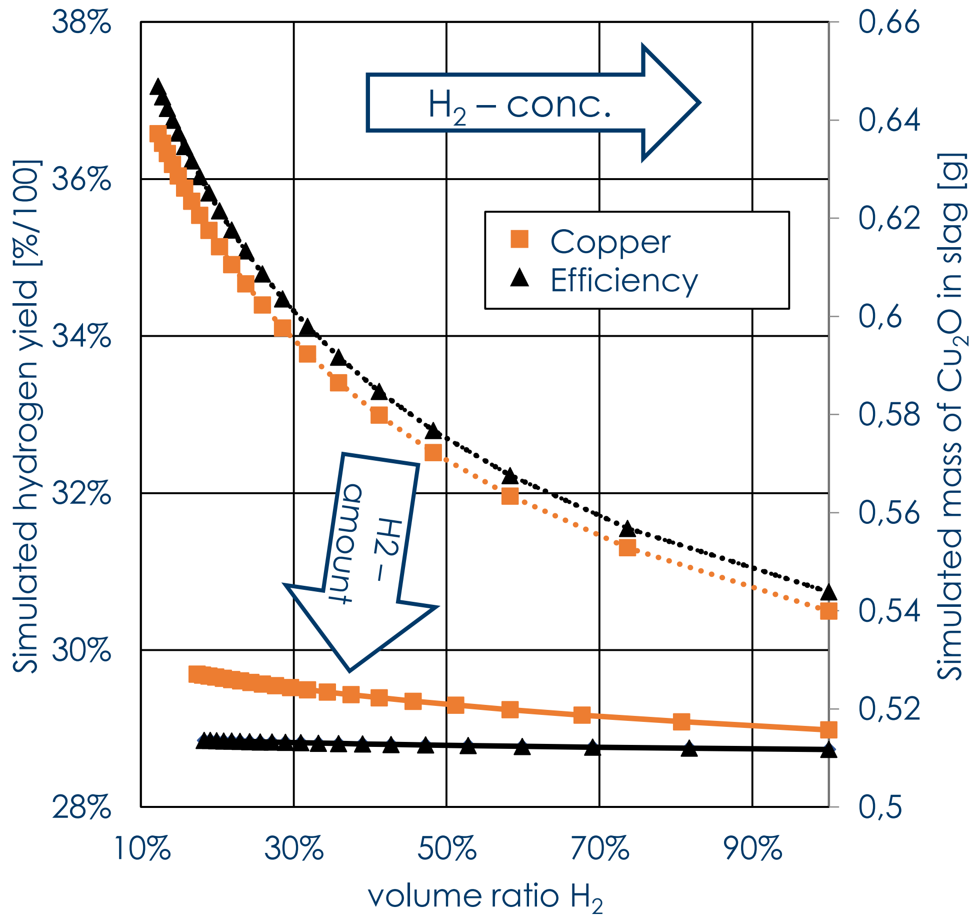
➢ Trials with higher H_2-amount cause low efficiency

simulation:

$$\eta_{H2} = \frac{H_2O_{product}}{H_{2\,injected}}$$

experimental:

$$\eta_{H2} = \frac{\sum Cu, Fe, Pb, Zn_{reduced}}{H_{2\,injected}}$$



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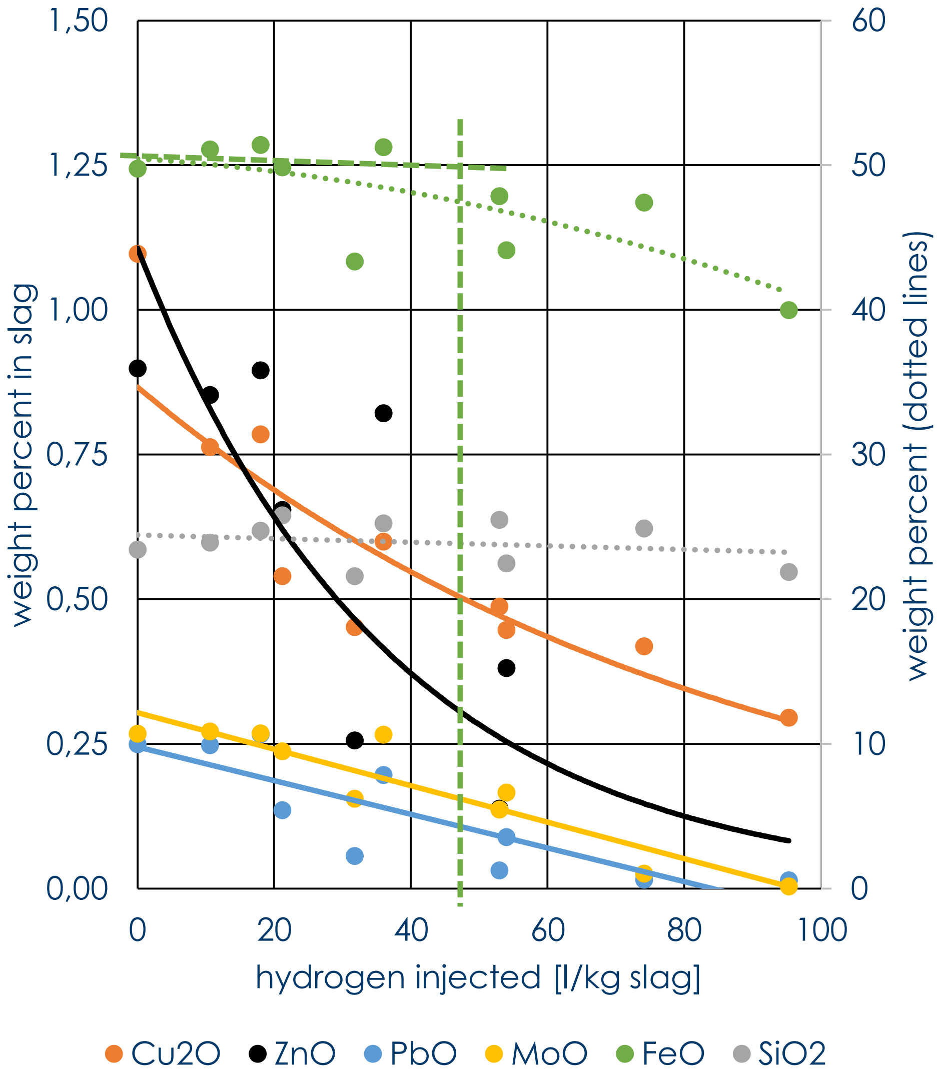
Evaluated trials
chemical analysis

- Copper decreased to 0.5 wt.% Cu_2O
  - With low FeO reduction
- Lead and zinc decrease to ∑< 0.2 wt.%
  - White and yellow powder in flue dust
- ~10 g metal/kg slag
  - <60 % Cu, 25 % Fe
  - Weight percents of Sb, Mo, Ni, As, Sn



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Conclusion

- Selective reduction possible
  - > 0.5 wt.% Cu_2O
  - Max. 73 % Cu-reduction
- Hydrogen yields 10 – 17 % in lab scale
  - Low melt column and residence time
- Fuming of slags possible to low contents of ZnO and PbO < ∑0.1 wt.%

Outlook

- ➢ Influence of H_2-concentration
- ➢ Influence of lime addition
- ➢ Kinetics of hydrogen reduction
- ➢ Upscaling of trials to 300 kg (40 cm slag column)
  - 4 t at Aurubis AG Hamburg (70 cm slag column)

Further publications

- Slag valorization symposium 2023, Belgium
- European metallurgical conference 2023, Germany

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Thank you

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