



Thermodynamics of phosphorus recovery

GTT Workshop 2015
Sander Arnout, InsPyro

www.RecoPhos.org

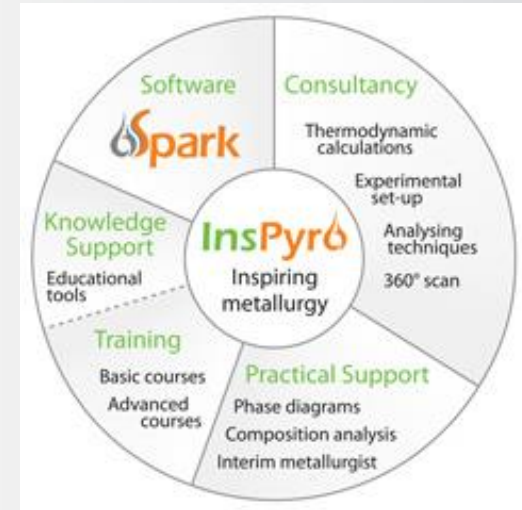
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KU Leuven spin-off (2009)
Founded and run by PhD's
B2B consultancy company

- Process development and improvement through:
 - Modelling and literature
 - Experiments
 - Characterization
 - Industrial experience
- Industries:
 - recycling incl. batteries and residues
 - non-ferrous metallurgy (lead-zinc)
 - steel, cast iron and ferro-alloys
- www.inspyro.be

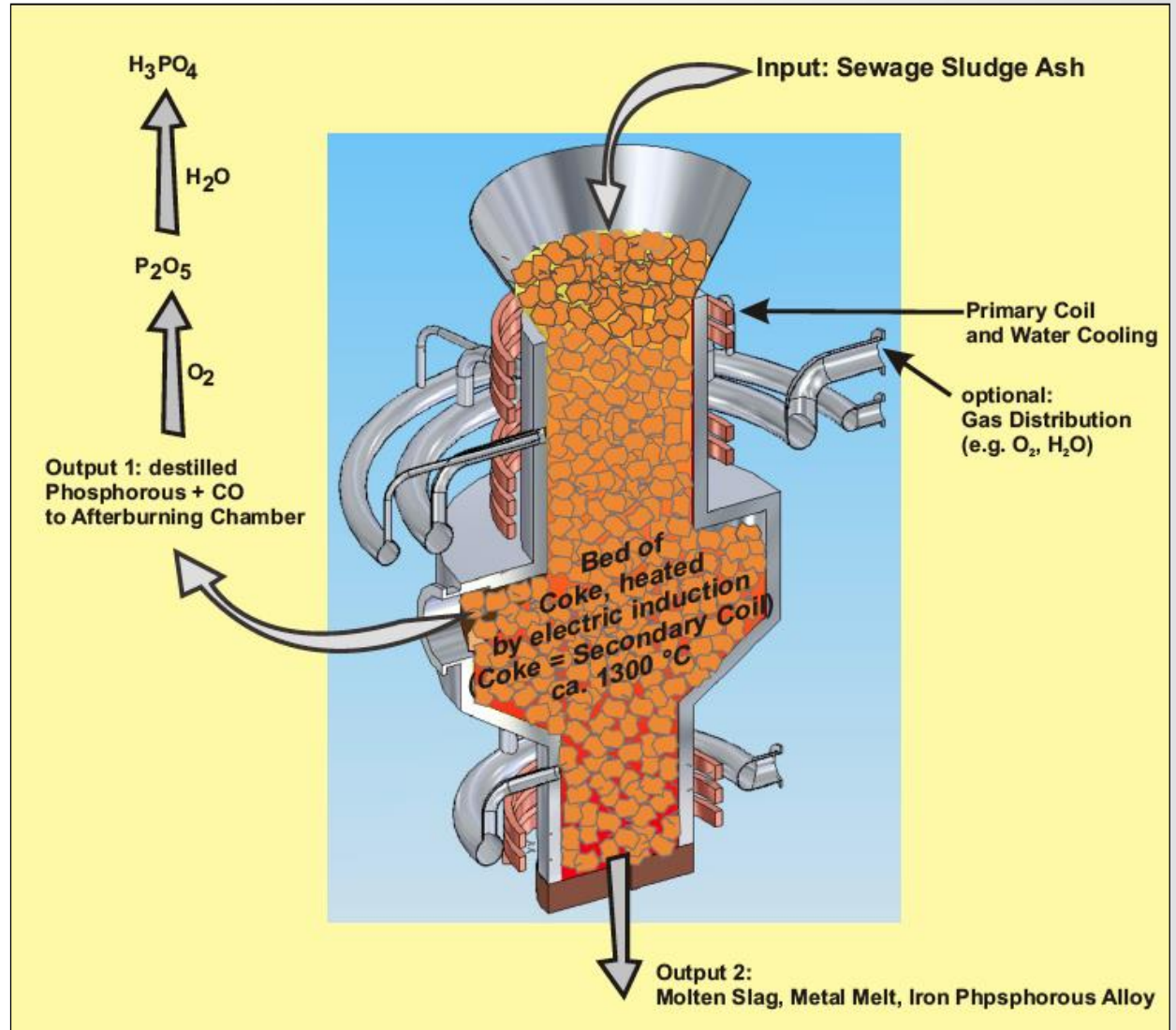


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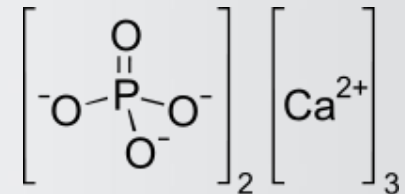
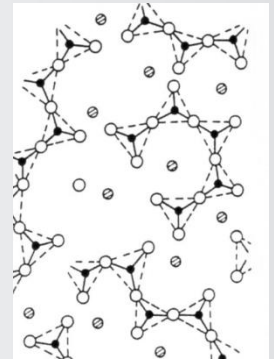
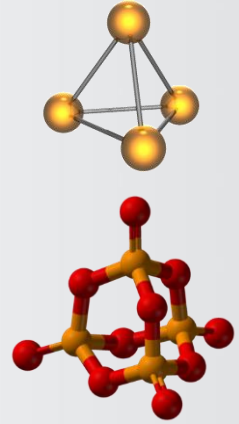


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To understand the RecoPhos process, we need to know the behaviour of P in all phases:

- Gas
 - $P_4(g)$, but also $P_2(g)$, P_4O_{10} , $PO_2...$
- Metal
 - Fe-P-Si-... liquid, Fe_3P upon cooling
- Slag
 - A network former like SiO_2
 - Strong interactions in phosphate stoichiometry e.g. $Ca_3(PO_4)_2$

The formed equilibrium is a result of activities of P compounds in all 3 phases.



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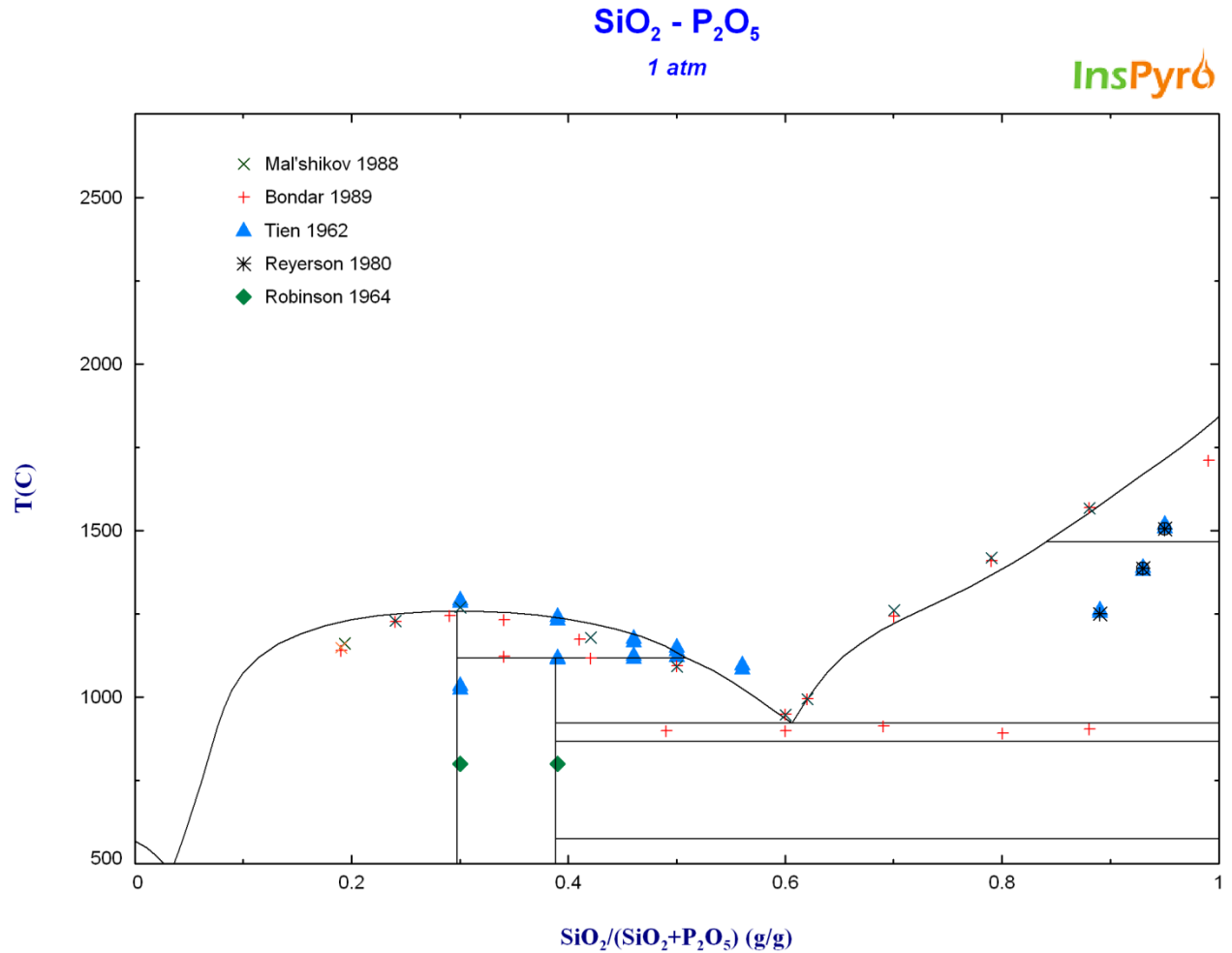
- State-of-the-art thermodynamic descriptions:
 - Most gas components available
 - Liquid metal phase and intermetallics OK
 - Slag with high P **not available**
- System P_2O_5 -CaO-SiO₂-Al₂O₃-FeO-Fe₂O₃ as basic scope
- Need for full model of systems with P_2O_5

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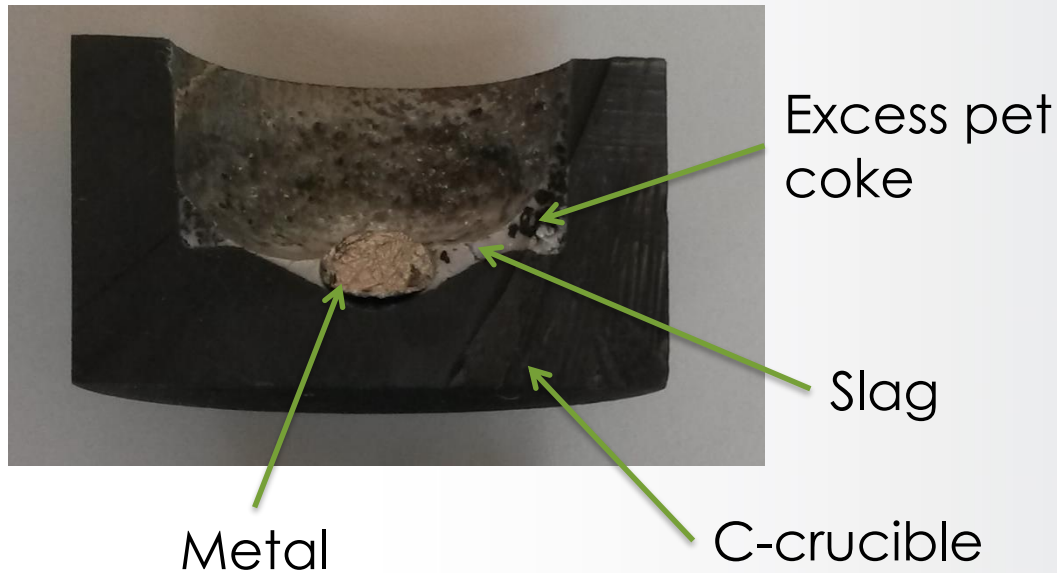
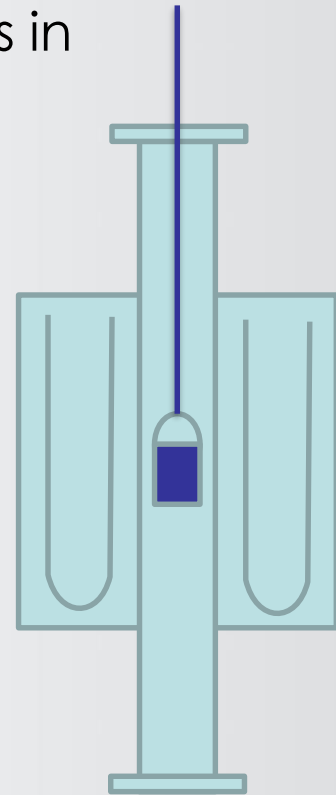


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- Goal: provide model validation points in controlled equilibrium state
- Conditions: Ar, 1400-1600°C, 4h
- Fluxing with SiO_2 and CaO
- Carbon saturation

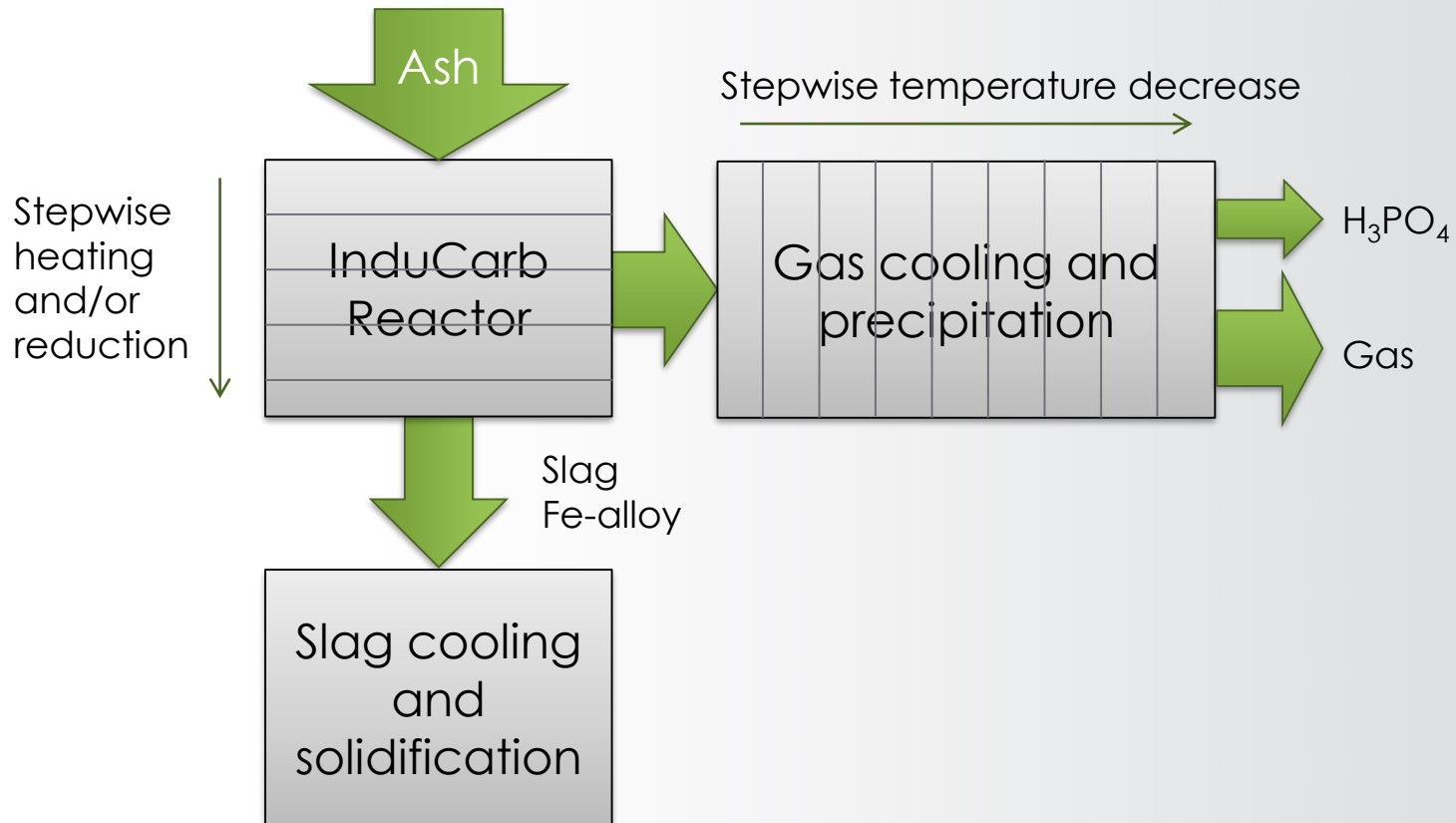


- Macroscopic process model
- Different equilibrium steps

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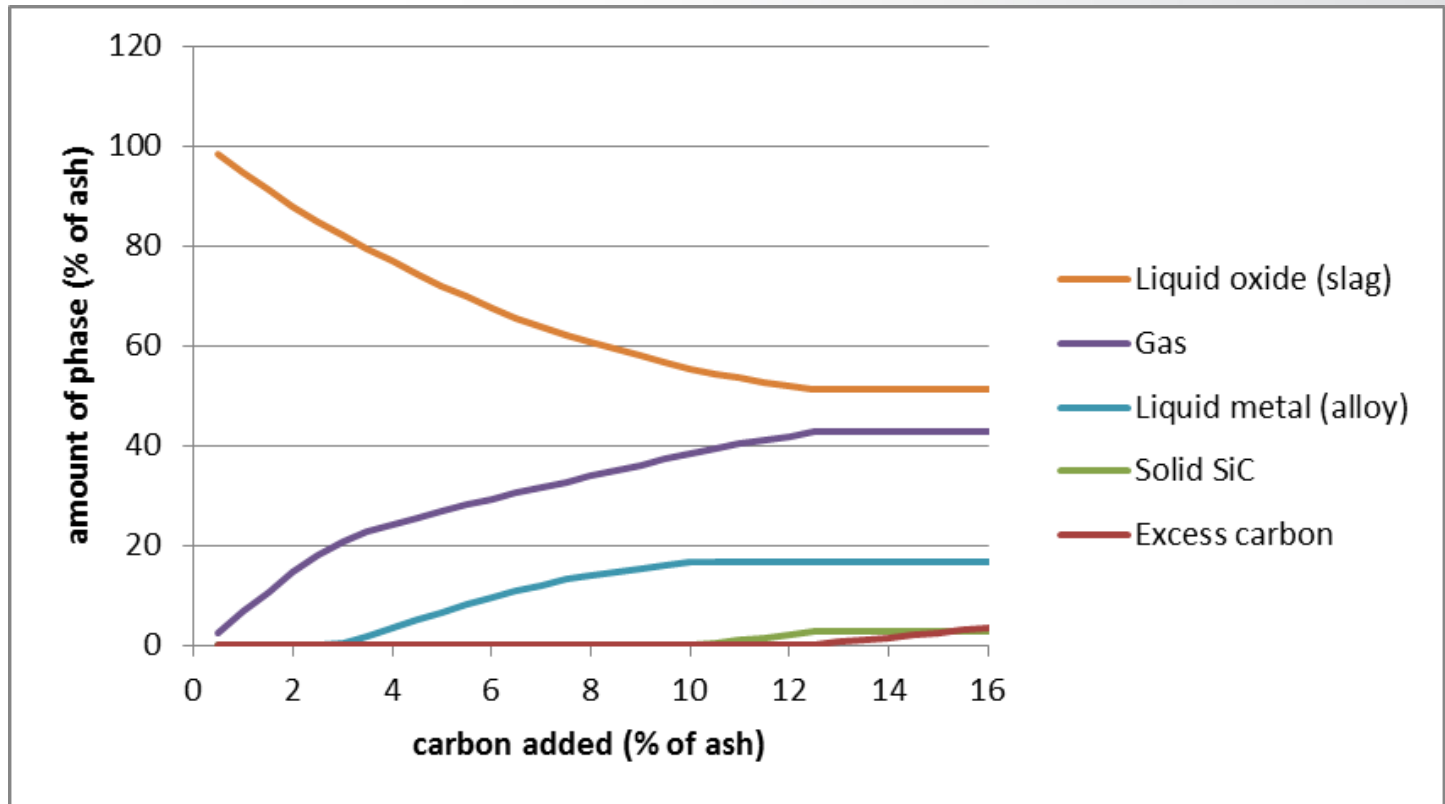
- Fuming model predicts phases and compositions as a function of reduction

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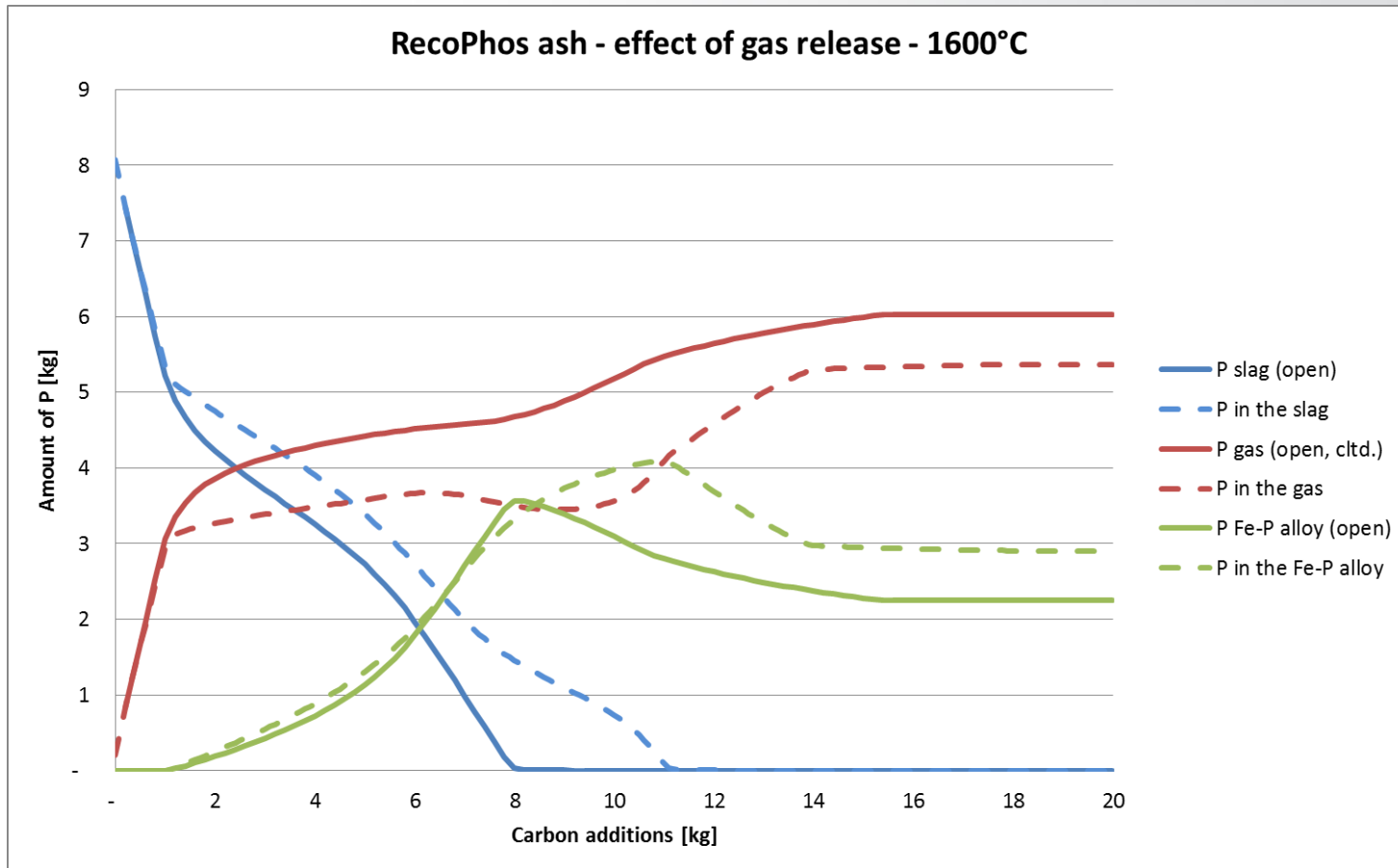
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RecoPhos ash - effect of gas release - 1600°C



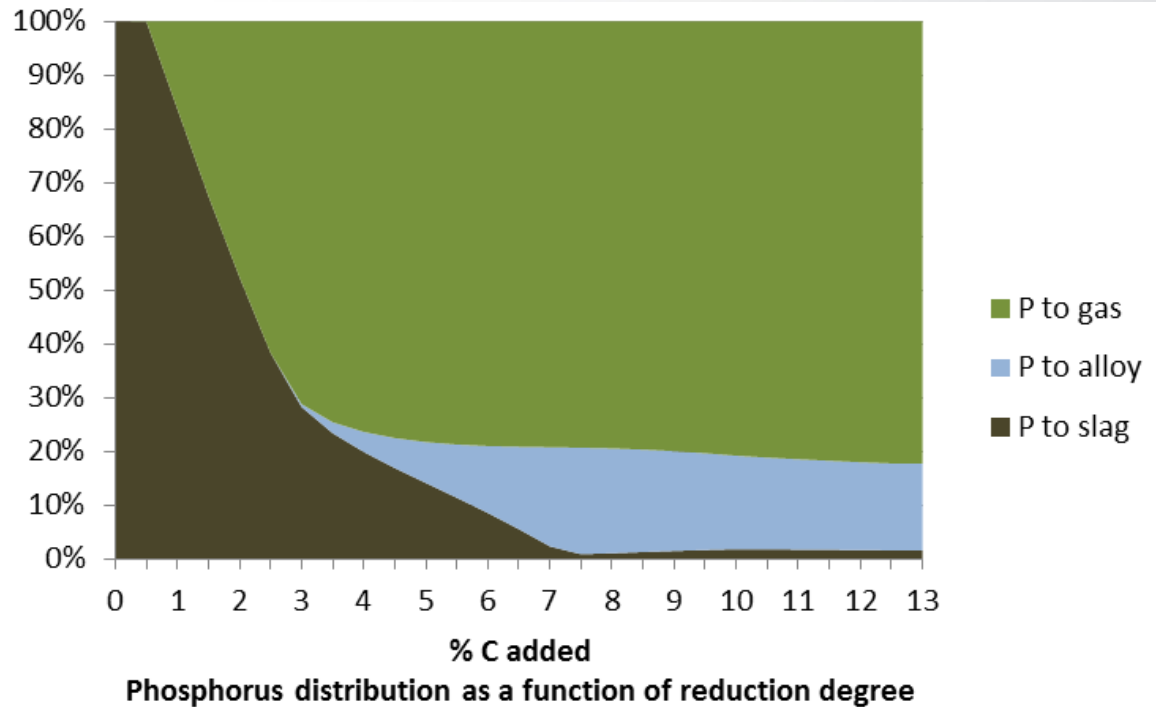
- The effect of reduction degree, basicity and temperature on the behaviour of phosphorus be can precisely studied

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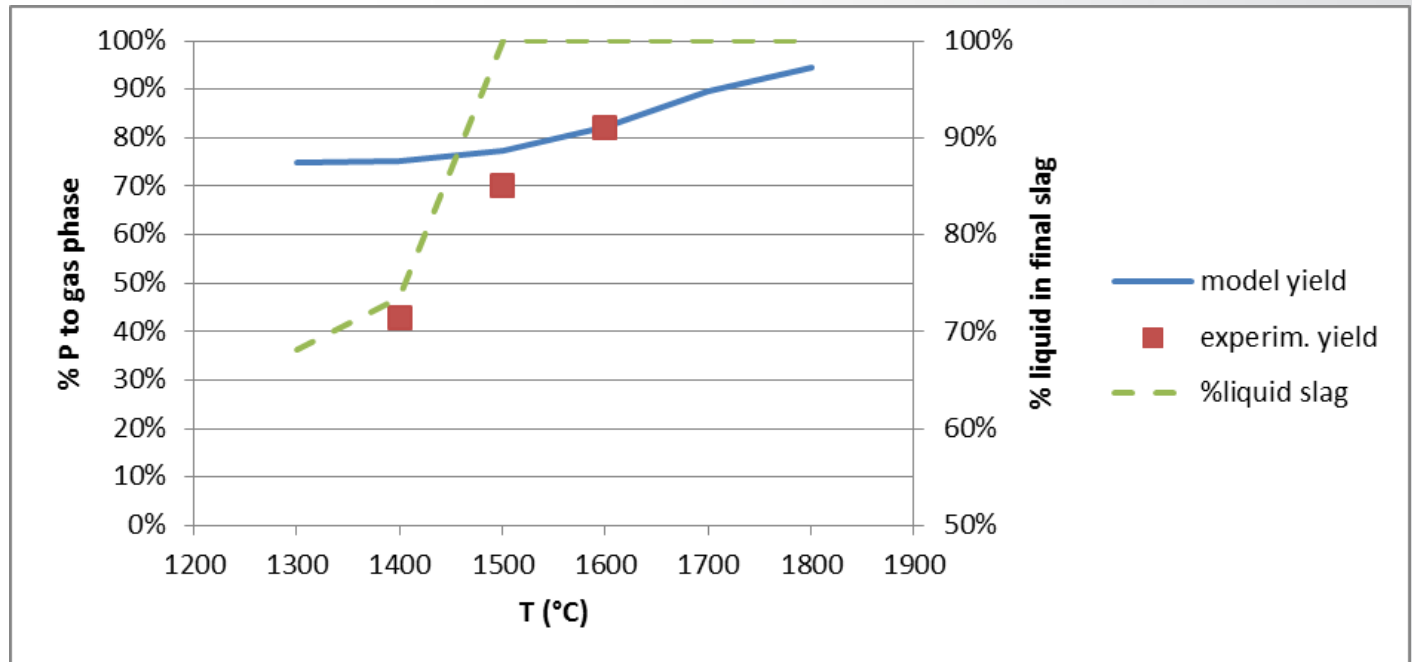
- Temperature effect:
 - Good agreement at high T (extrapolation)
 - Lower temperature lowers P yield
 - Quicker decrease in experiments, probably reaction speed, ~ liquid fraction final slag

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- Demo reactor: number of experiments limited
- Clear influence of basicity:
 - Natural slag is low C/S and highly viscous
 - Reduction and flow can be optimized by fluxing with CaO
 - With better flowability, good agreement with modelled equilibrium
- Even with short residence time, thermodynamic model provides a good framework
 - Composition of all phases in good agreement
 - Mass balance and overall yield

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- Predict precipitation upon cooling
 - Precipitation temperatures allowing thermal design and separation
 - Impurities as phosphates or sulphates
 - Form of P as a function of conditions
- Assume equilibrium or Scheil cooling
 - Enable or disable further reaction of precipitated solids

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- Predict high temperature behaviour:
 - Viscosity
 - Melting point
 - Solid phases present
 - Starting ash and final slag have different properties!
- Predict solidification and low temperature mineralogy
 - Link to cementitious properties
 - Slag as largest volume product

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- Evolution of melting point during reduction

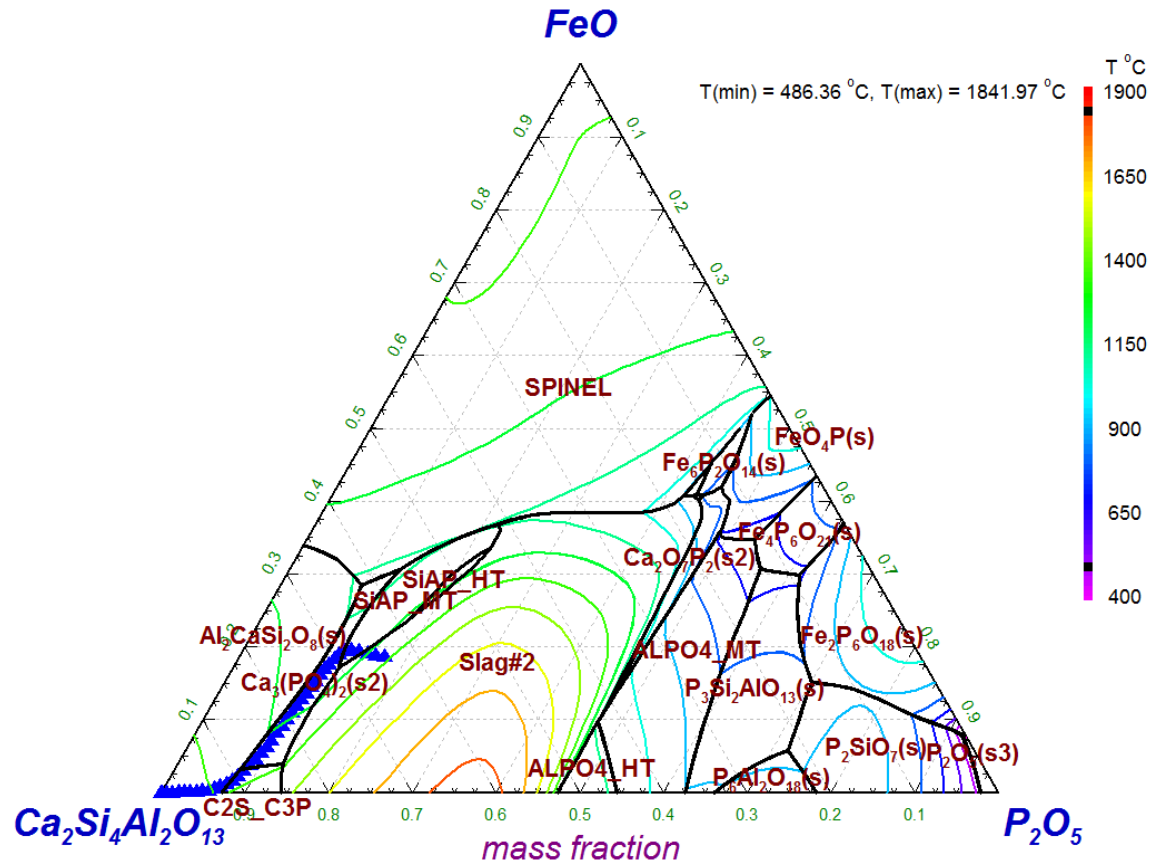
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Ca₂Si₄Al₂O₁₃ - FeO - P₂O₅ - O₂
Projection (Slag), p(O₂) = 10⁻⁶ atm, 1 atm

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- Recovering P from sewage sludge is possible
- Understanding the chemistry is an essential need for a successful high temperature process
 - P yield and quality
 - Slag behaviour and quality
 - Expected alloy formation
- The models have shown good agreement with experimental results

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