RecoPhos

Phosphorus in slag and modelling of the RecoPhos process

Bastien Soete, Sander Arnout, Els Nagels

InsPyro

- What do Babe and a coke have in common?

Contents

- The Recophos project
- The RecoPhos process
  - Wöhler process
  - Ash reduction
  - InduCarb reactor
- Phosphorus in the slag
  - Phosphorus and its modelling
  - P_2O_5 containing systems
  - P_2O_5 – CaO – SiO_2
- Process modelling
- Conclusion

The RecoPhos project

- The phosphorus cycle

Phosphate rock
Fluorapatite
$Ca_{10}(PO_4)_6F_2$

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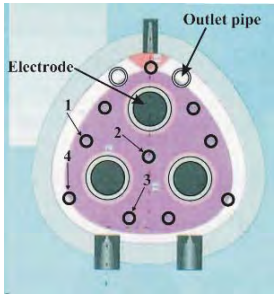

Whoëler process
Submurged arc furnace

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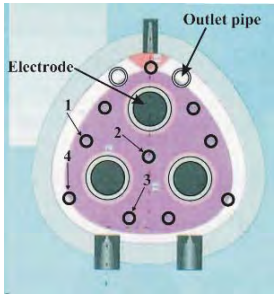

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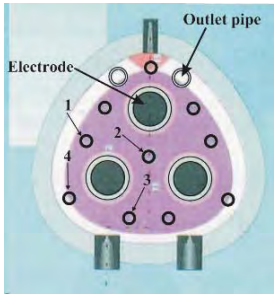

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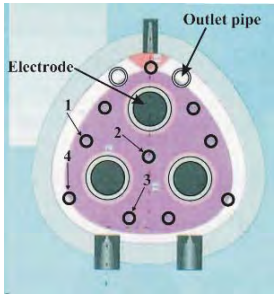

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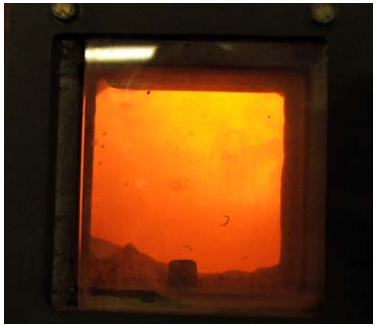


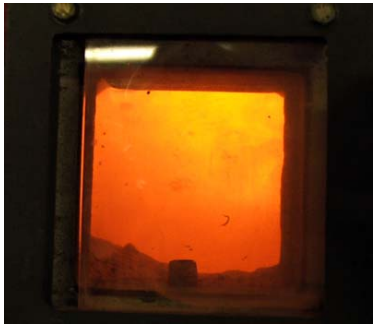
Energy recovery

The RecoPhos project

- The phosphorus cycle

Landfill

Sewage sludge



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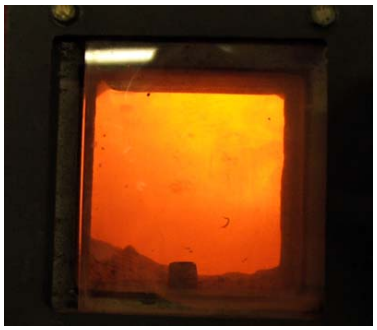
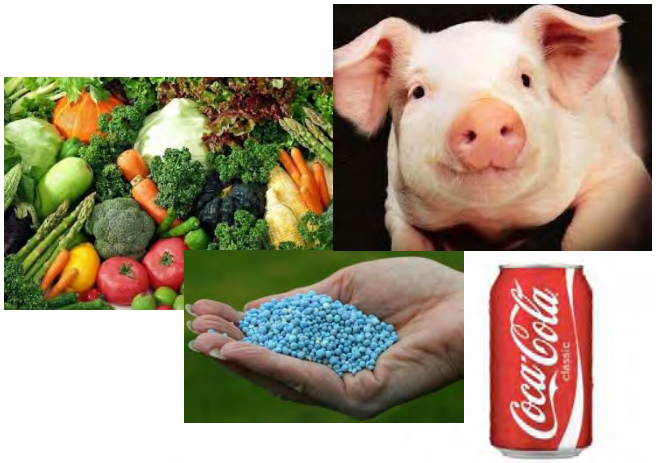


Energy recovery

Ashes

Closing the cycle for P



P-containing products

RecoPhos

InsPyro

Inspiring metallurgy

RecoPhos

The RecoPhos project – 10 partners

MONTAN UNIVERSITÄT
WWW.UNILEOBEN.AC.AT

Universität Stuttgart
iswa

GCTU
Gesellschaft für Chemischen und Technischen Umweltschutz mbH

SGL GROUP
THE CARBON COMPANY

TPT
Thermoprozesstechnik

InsPyro

Hariri
Chemical Process Engineering
C P E

M·A·L
www.mal.at

INERCO

M.I.T.

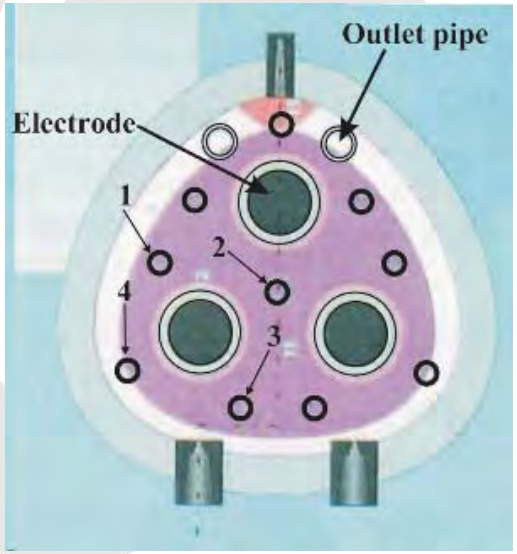
jeloga
Engineering

The RecoPhos process

- Similar to Wöhler process (submerged arc furnace)
  - Input: phosphate ores (15-20% of fluorapatite; 7-10%P_2O_5)
  - Reaction: vaporisation of the P

$$Ca_{10}(PO_4)_6F_2 + 15C + 9SiO_2 \rightarrow 3P_2(g) + 9[(CaO.SiO_2)] + CaF_2 + 15CO(g)$$

  - Output: gas treatment
    - Pure P in inert atmosphere
    - Oxidation to P_2O_5 or phosphoric acid H_3PO_4



The RecoPhos process

- Reduction of phosphorus oxide and evaporation of P
  - From sewage sludge ash:
    - Composition

Ash content	Weight %
P_2O_5	15-25
CaO	12-15
SiO_2	5-20
Fe_2O_3	2-30
Al_2O_3	2-20

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$$P_2O_{5\ (slag)} + 5\ C_{\ (s)} => P_{2\ (g)} + 5\ CO_{\ (g)}$$

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  - Possible reduction of Fe_2O_3

The RecoPhos process – Innovative reactors

- Developed for EAF dust treatment
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- InduCarb reactor
  - Where the reduction takes place
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- Developed for EAF dust treatment
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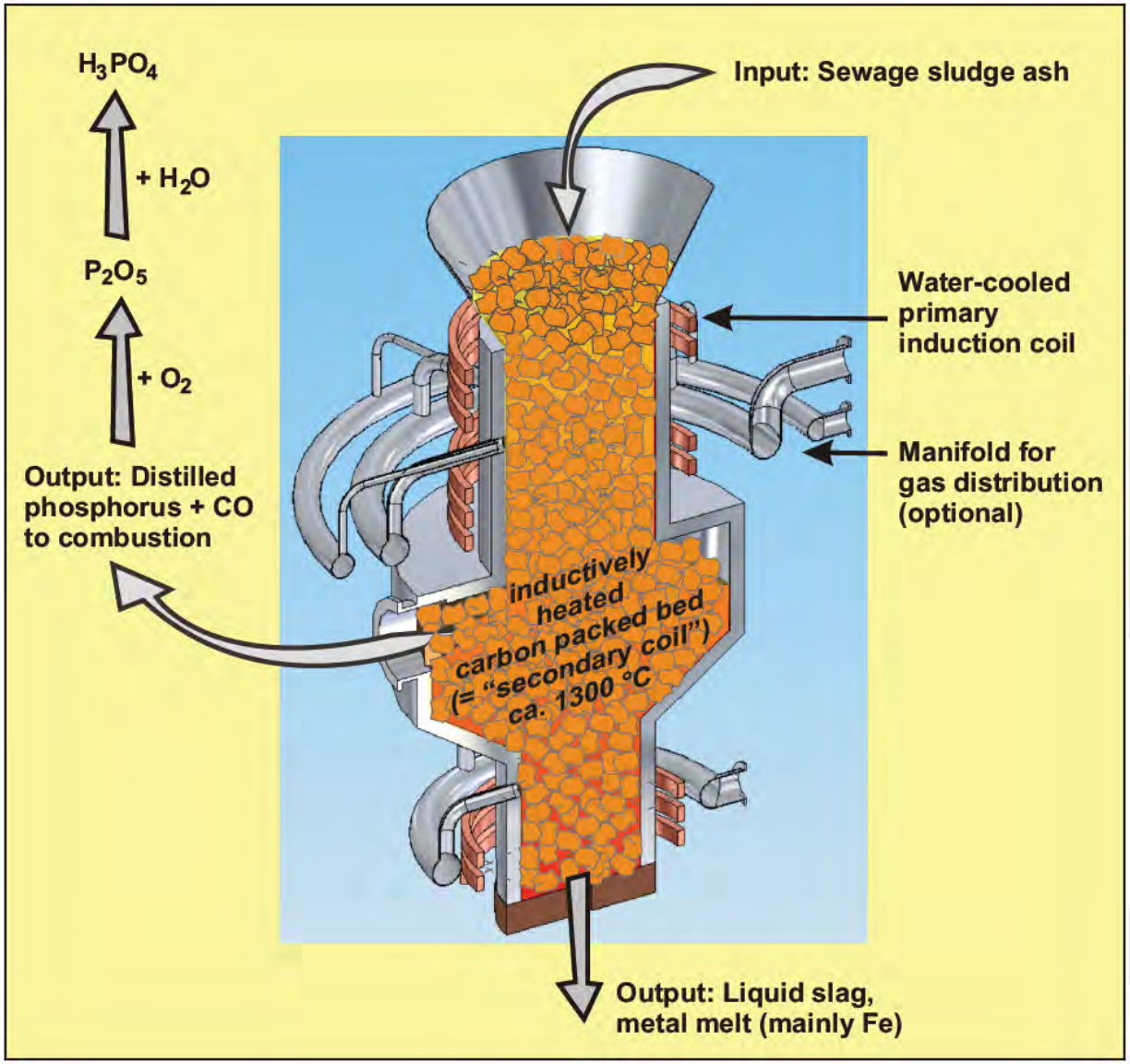
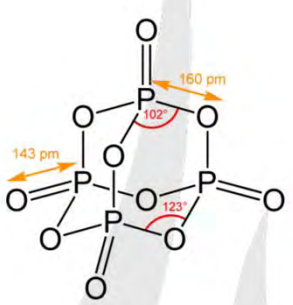
- InduCarb reactor
  - Where the reduction takes place
  - Packed carbon bed
  - Inductively heated
- Possible use of a flash reactor prior to InduCarb
  - Use organics (dried sludge) to generate heat for melting
  - Evaporate heavy metals (to be investigated)
  - Energy savings on the melting

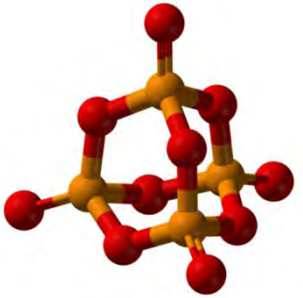
The RecoPhos process – InduCarb reactor



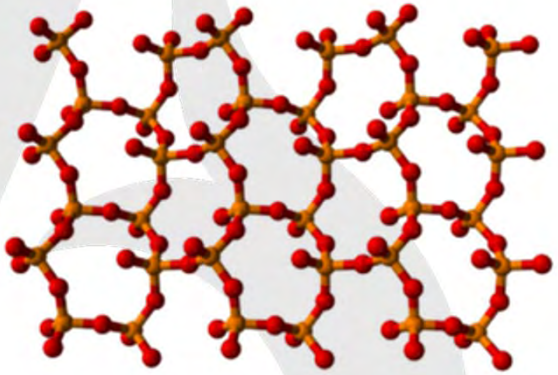
Phosphorus in slag

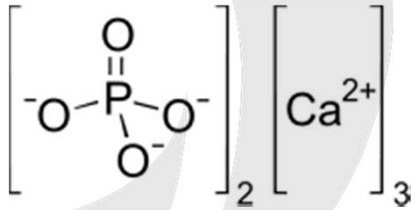
- Many polymorphs of
  - P (white $_{(s)}$, red $_{(s)}$, $P_{2\ (g)}$, $P_{4\ (g)}$…)
  - P_2O_5 (P_4O_{10} molecules, networks…)





- Oxide in slag:
  - As P_2O_5 (associate model, 2 metal atoms)
  - Network former:
    3 network bonds via O (+1 double to O)
  - Associates for ideal combinations
    such as $Ca_3(PO_4)_2$



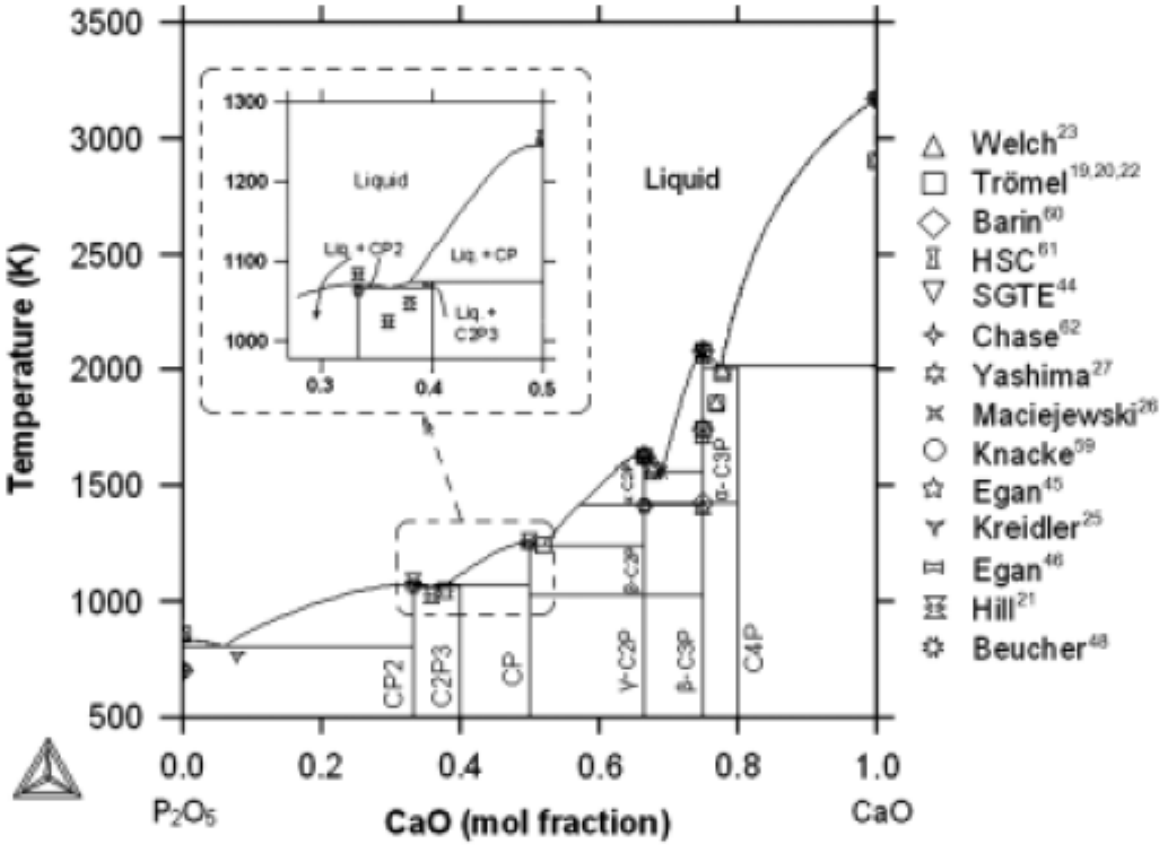


Phosphorus in slag – Systems to study

- Systems to be studied
  - Binary: P_2O_5 – CaO
    SiO_2
    Fe_2O_3
    Al_2O_3
    Na_2O
  - Ternary : P_2O_5 – CaO – SiO_2; P_2O_5 – CaO – FeO
    P_2O_5 – FeO – SiO_2; …
  - Quaternary
  - …
- Strategy
  - Find the relevant data in the literature
  - Develop the databases

$CaO-P_2O_5-SiO_2$ system

- Thermodynamic assessment by S. Serena in 2011

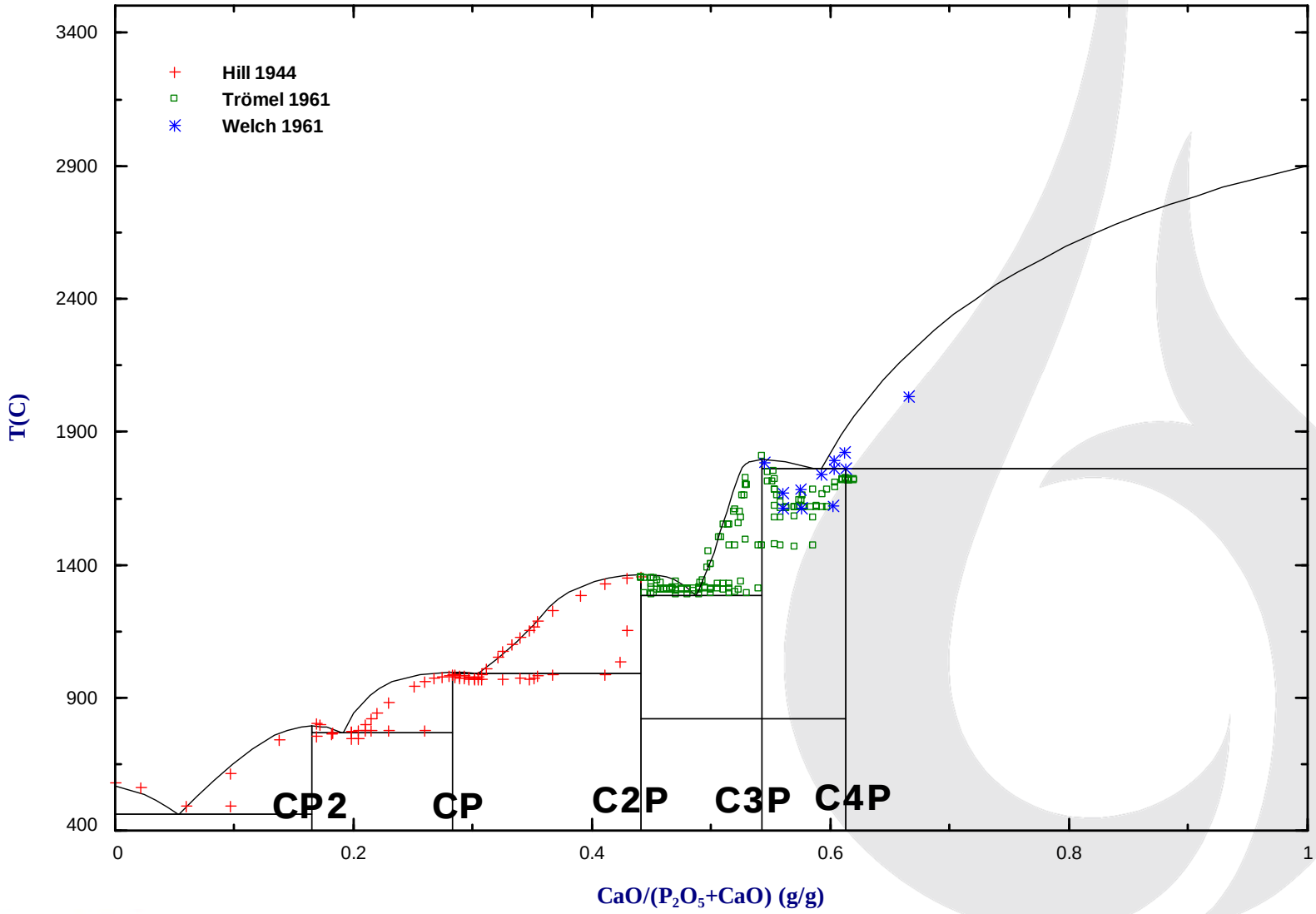


Complete description of intermediate compounds

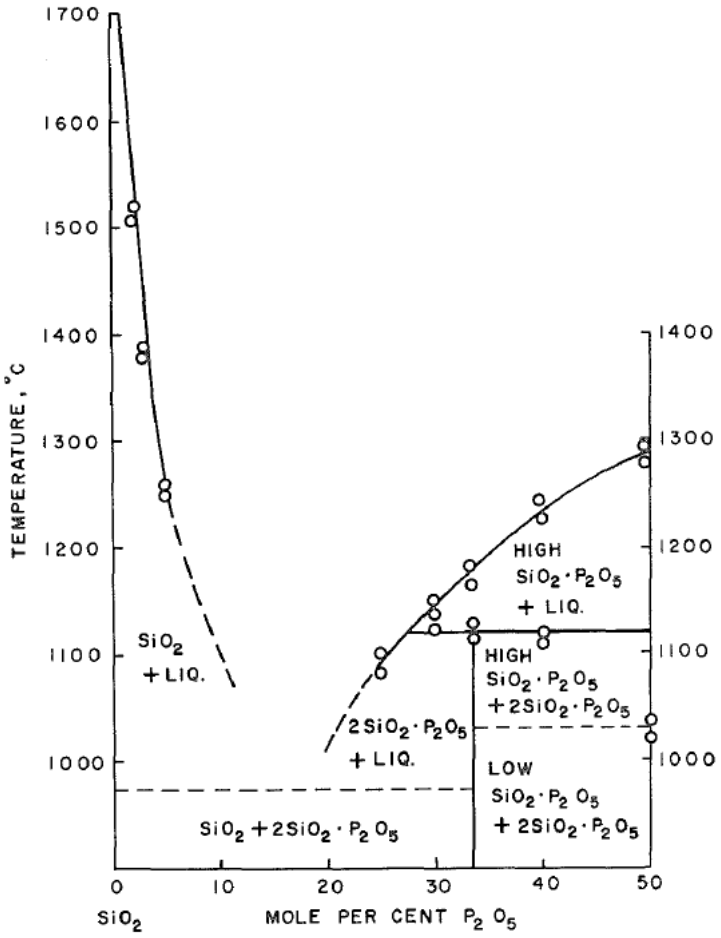
Liquid description using the two-sublattice model

Good starting point

$CaO\text{-}P_2O_5\text{-}SiO_2$ system

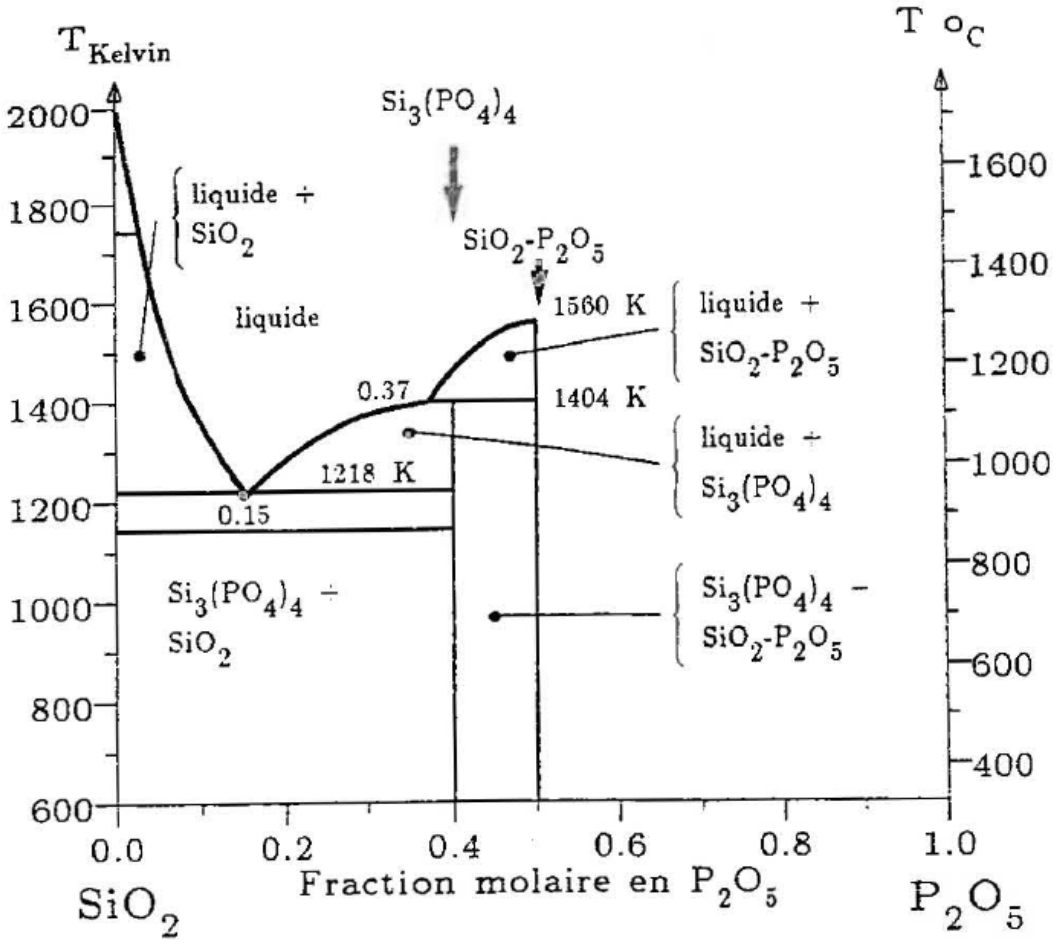


$CaO-P_2O_5-SiO_2$ system



T. Tien 1962

G. Baret 1991

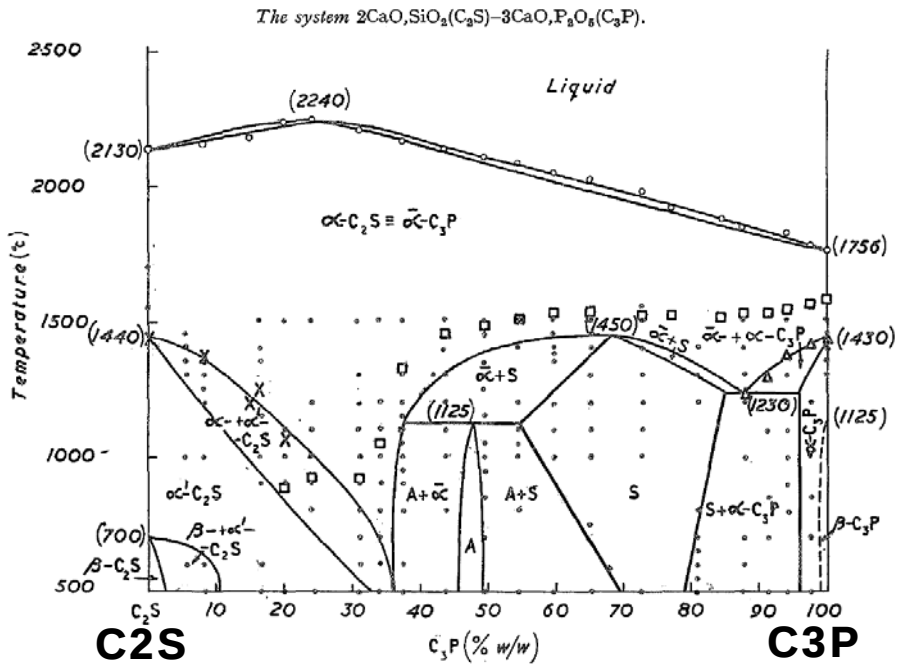


Excess enthalpy of the liquid phase

$$\Delta H = [13000 + 9000\ (1-2x)^2].Y.(1-Y)\ J.mol^{-1}$$

$CaO-P_2O_5-SiO_2$ system

Nurse 1959



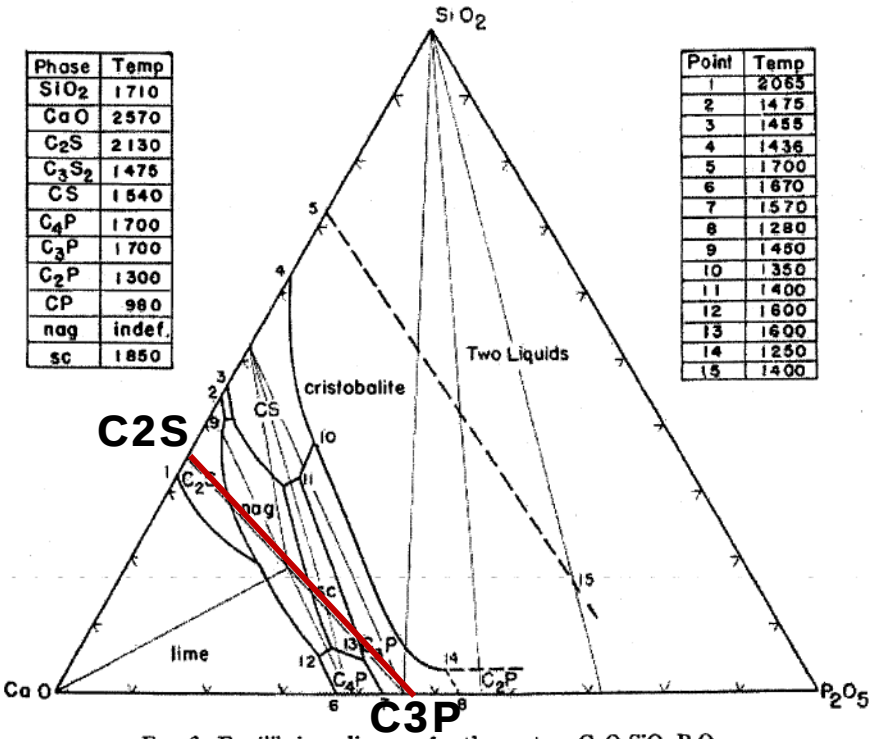


FIG. 3. Equilibrium diagram for the system $CaO-SiO_2-P_2O_5$. Temperatures are approximate.

Barrett 1942

Process modelling

- Reduction of ash
  - First model – P_2O_5 in slag as ideal solution
  - Give possible trends
  - Composition

Ash content	Weight %
P_2O_5	13
CaO	14
SiO_2	37
Fe_2O_3	13
Al_2O_3	15
O_2	8

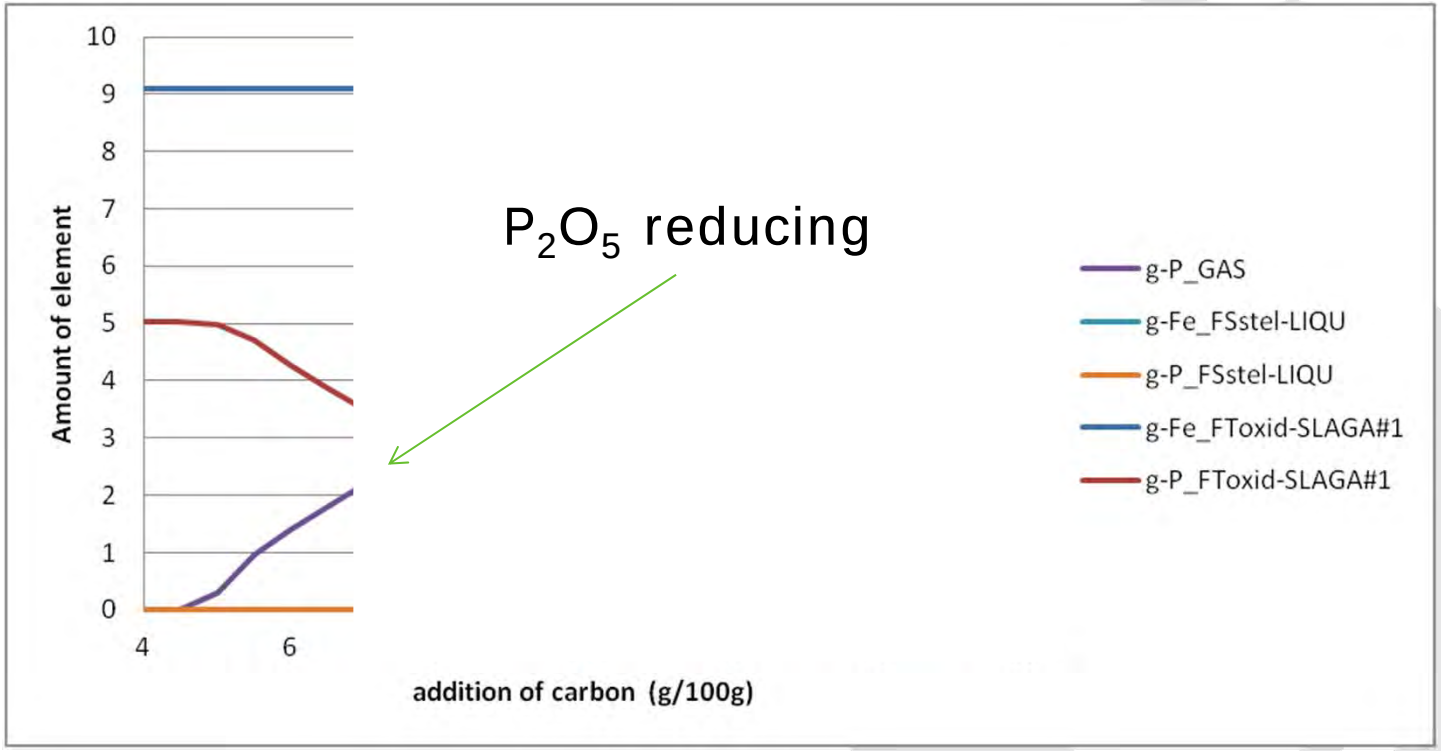
  - Operating conditions

    0 to 15 g C per 100 g of charge

    Temperature 1600°C

Process modelling (P ideal – 1600°C)

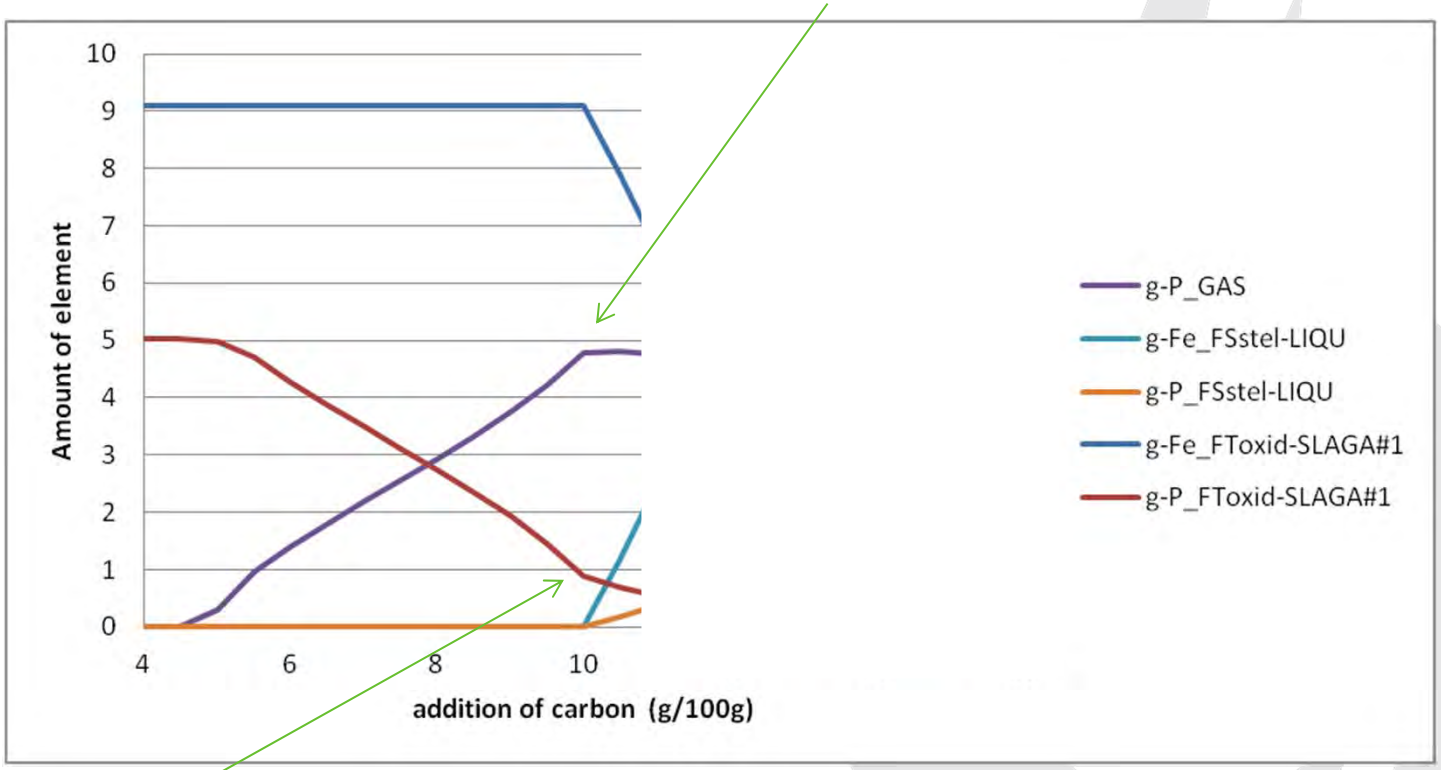
- Reduction: low carbon



Process modelling (P ideal – 1600°C)

- Reduction: optimal carbon

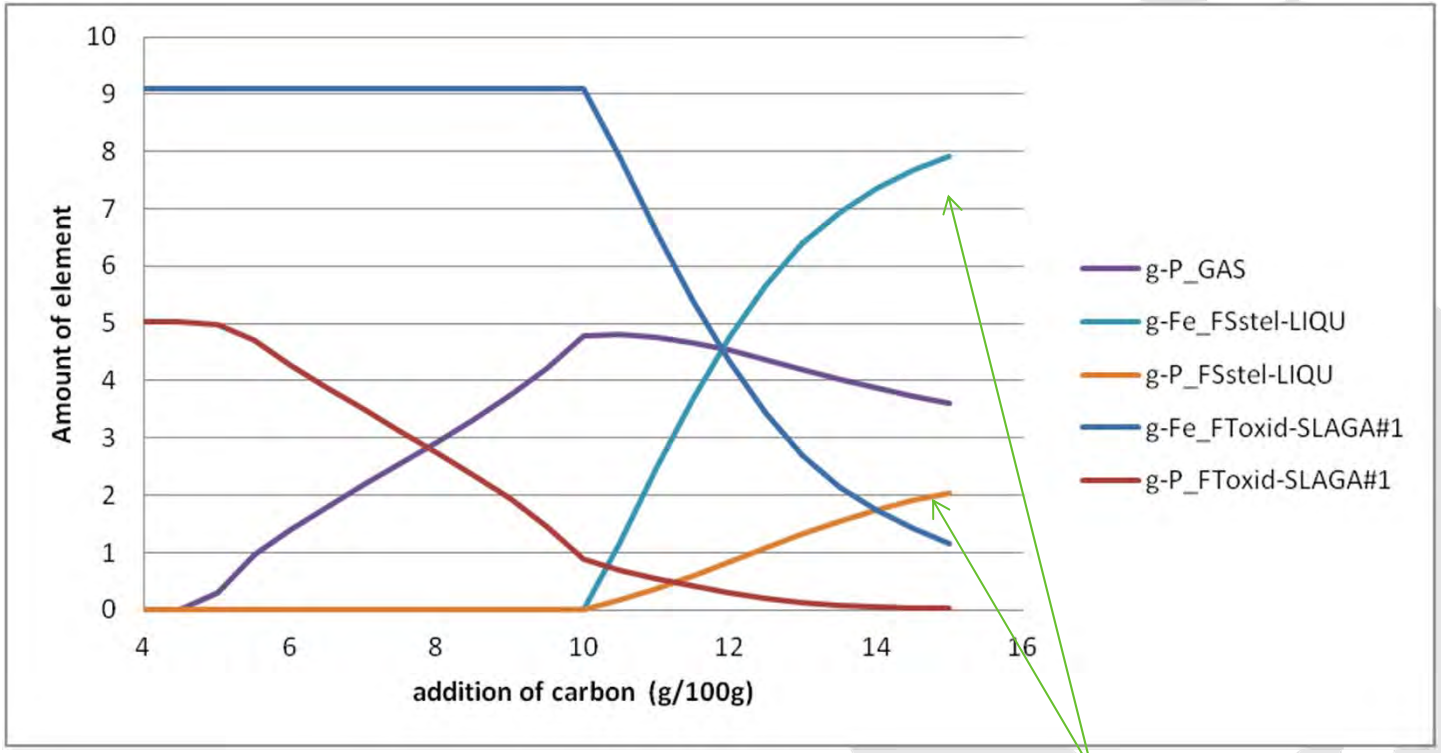
Optimal evaporation of P: just before Fe reduction (can this be controlled?)



Some loss of P in the slag

Process modelling (P ideal – 1600°C)

- Reduction: high carbon

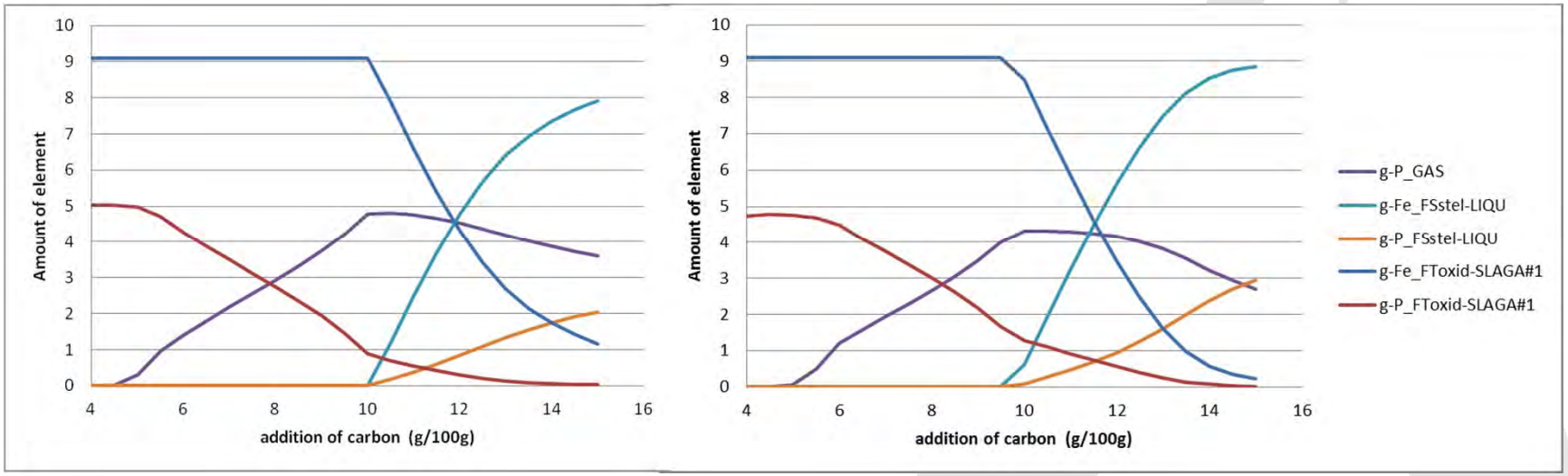


Presence of more iron in sludge
=> more Fe-P formation possible

Process modelling (P ideal)

- Reduction – temperature dependence

1600°C 1400°C



- Higher T = higher P recovery
- Induction heating could generate more evaporation
- Temperature in Wöhler process 1200-1400°C
- We may reach 1600°C

Conclusions

- RecoPhos
  - Closing the cycle on the phosphorus use
- Oxide database (associate model)
  - $CaO\text{-}P_2O_5$ started
  - Work in progress for the other systems
  - Will allow the process modelling
- Process model
  - Only ideal solution at present – simplification
  - Trends observed:
    - Temperature effect
    - Reduction effect on P-recovery