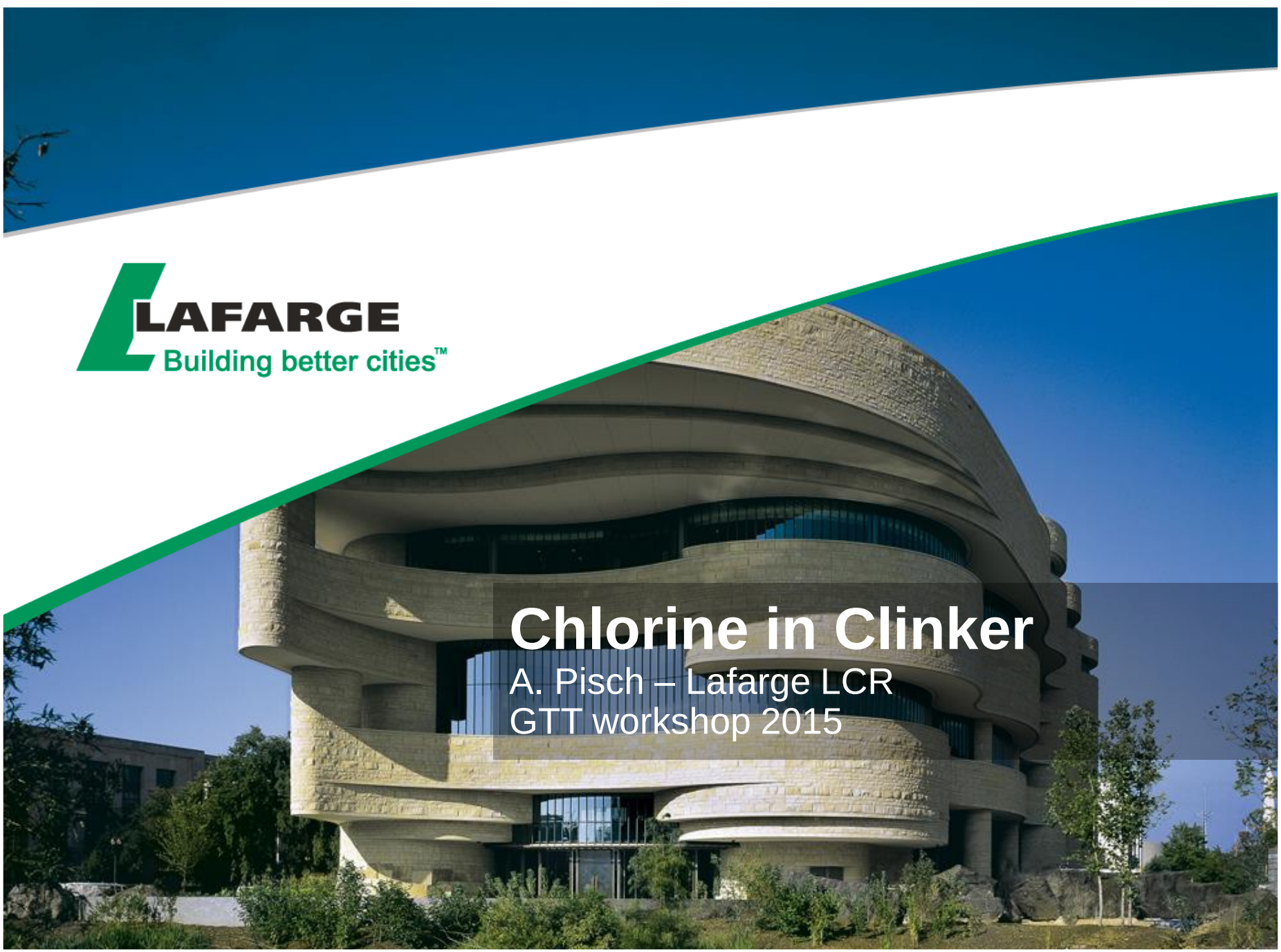

Chlorine in Clinker

A. Pisch – Lafarge LCR

GTT workshop 2015

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The cement making process

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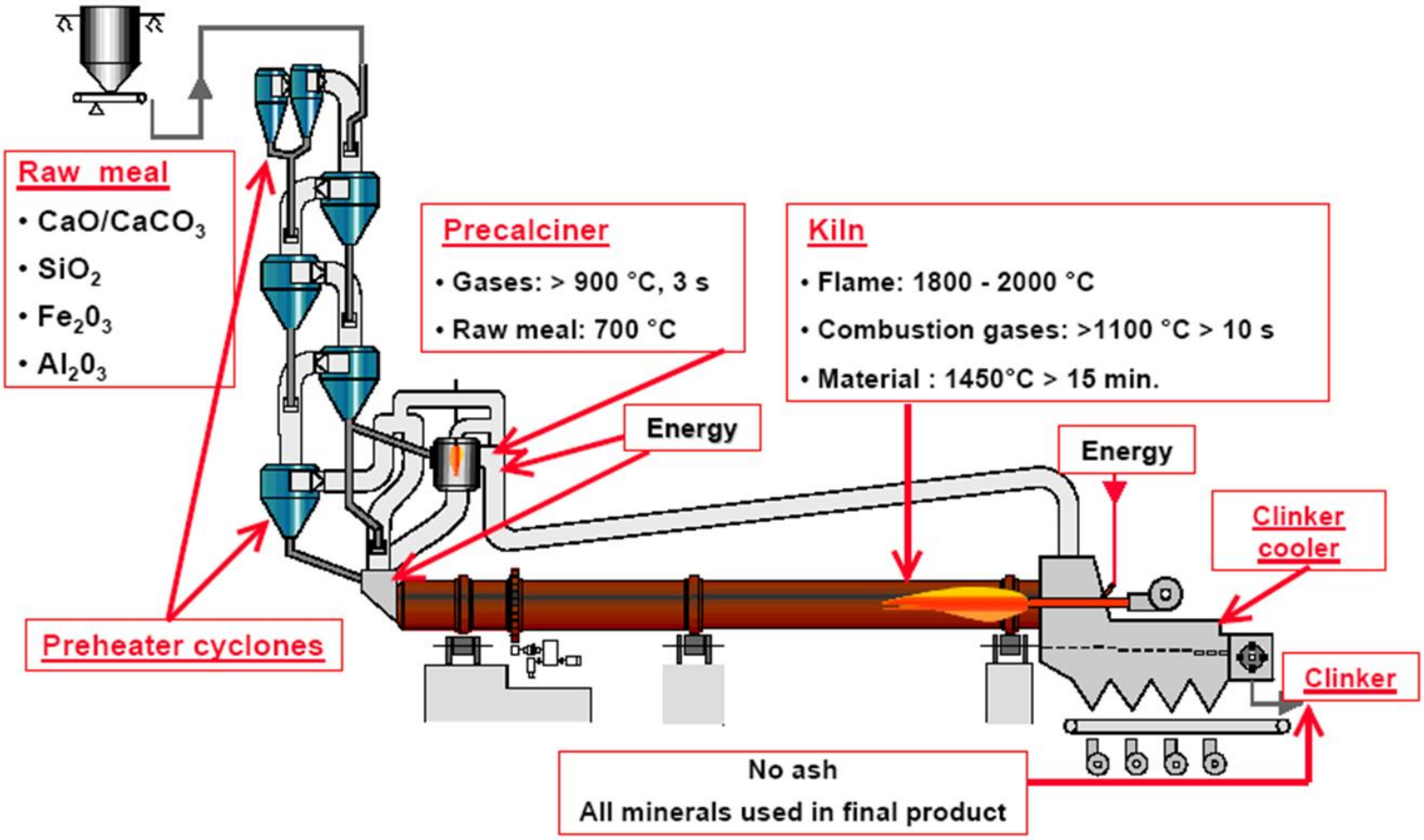


Origine of Chlorine in clinker

- **Two potential inputs for chlorine**
  - Raw materials
  - Fuels
- **Raw materials**
  - Input from raw materials is small (few ppm)
  - Alternative raw materials (mineral sludge…) may have higher levels
- **Fuels**
  - Input from classical fuels is low (coke, petcoke, gas…)
  - Input from alternative fuels is high (% range)

Alternative fuels

Biomass

Coffee husk

PKS: Palm Kernel Shells

Sunflower seed shells

Alternative fuels

Plastics

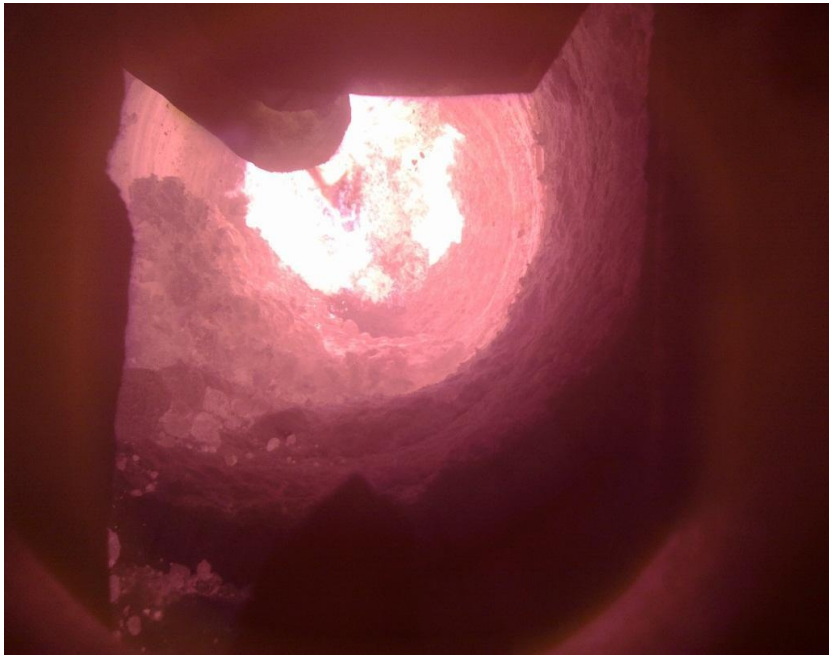
Plastic pieces

Shredded tyres

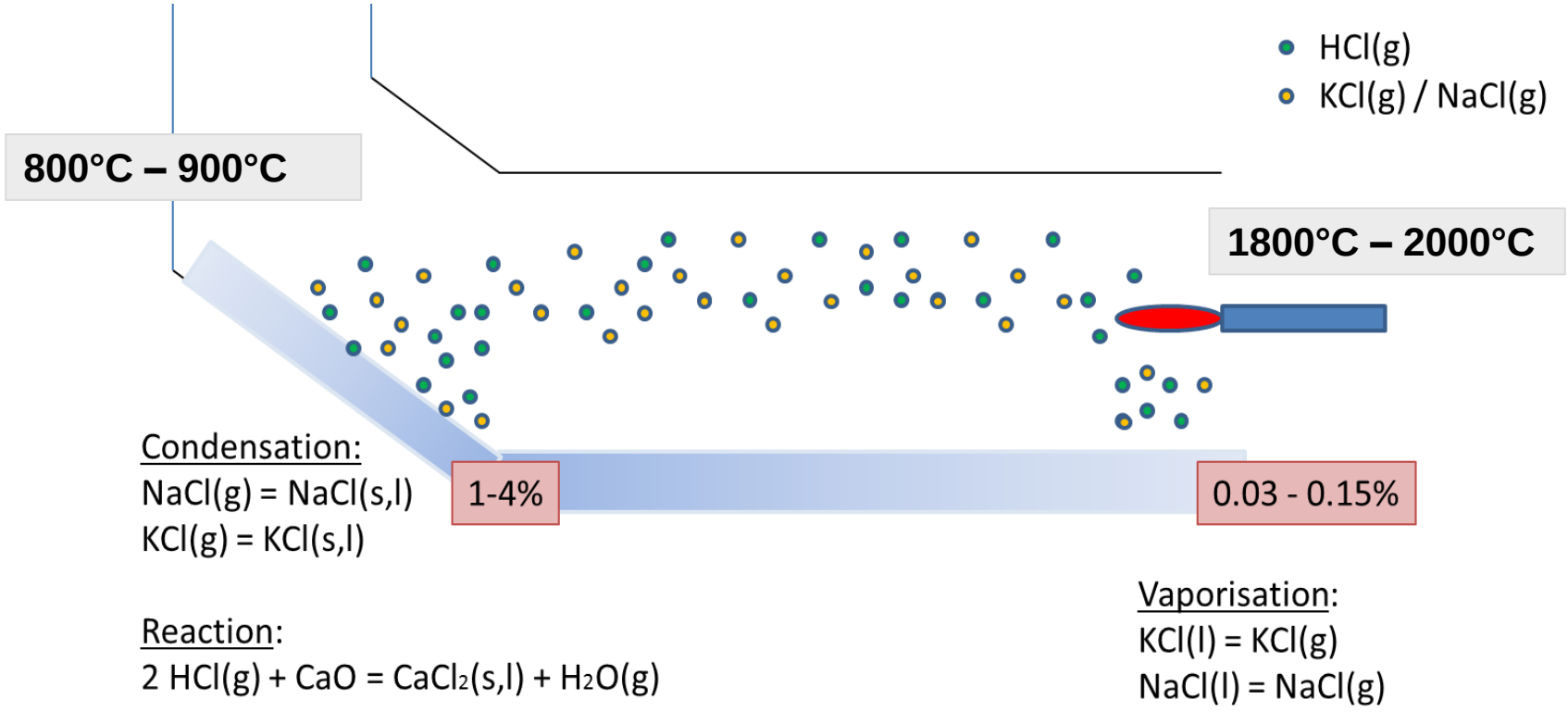
Shredded municipal waste

Alternative fuels

Burning

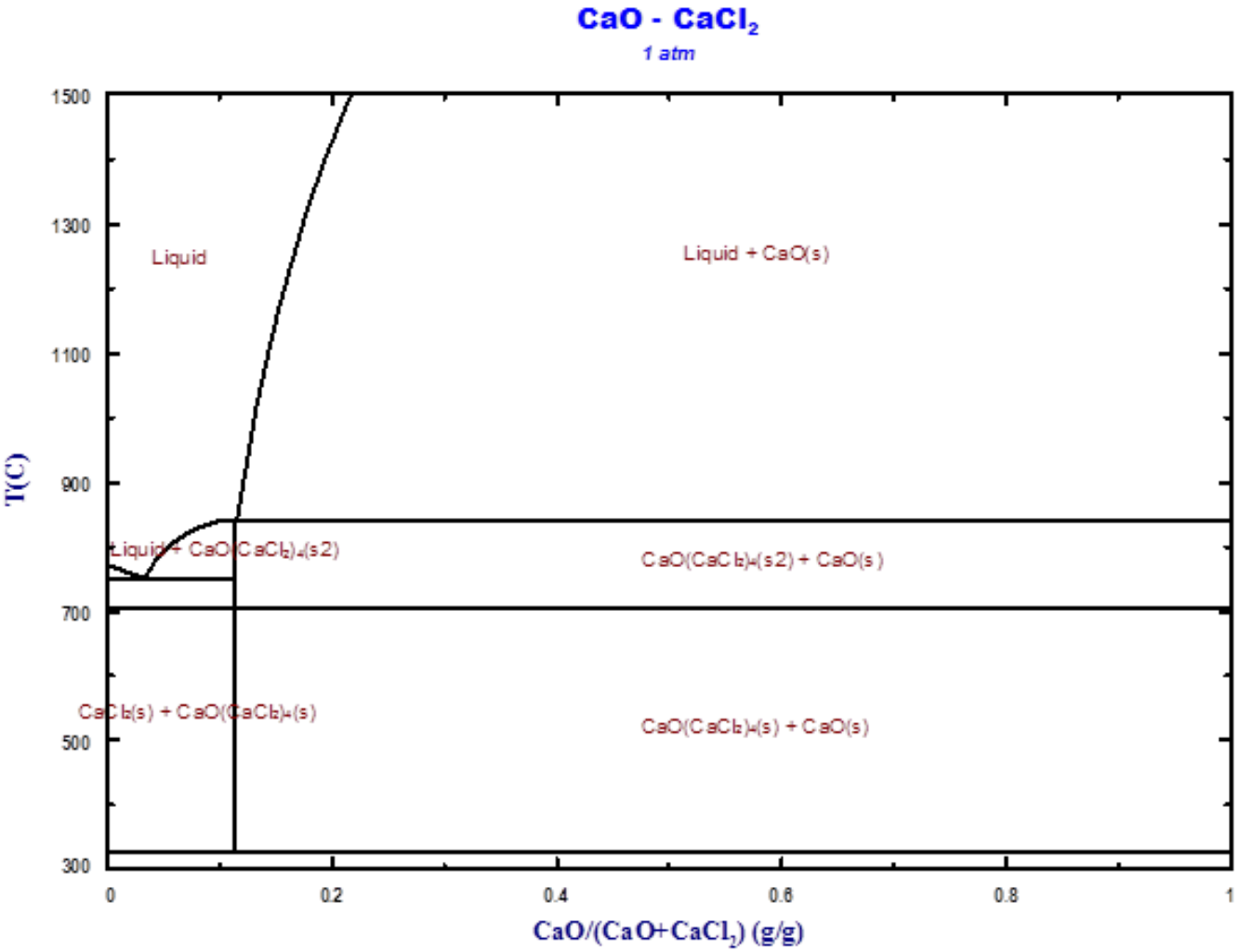


Chlorine cycling in a rotary kiln



Chlorine cycling in a rotary kiln

Kiln inlet

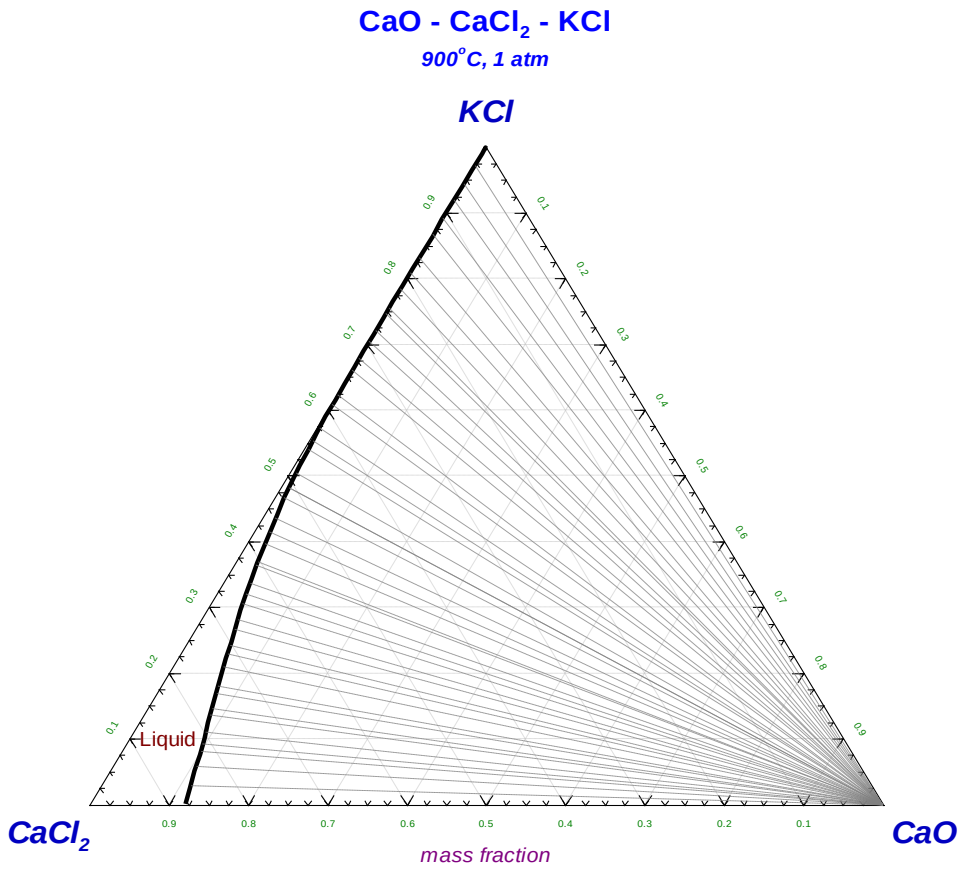


1% of Cl
=
1.9% of liquid

p_{HCl} = 4.3 mbar
@900°C

Chlorine cycling in a rotary kiln

Kiln inlet



Solubility of CaO decreases with KCl

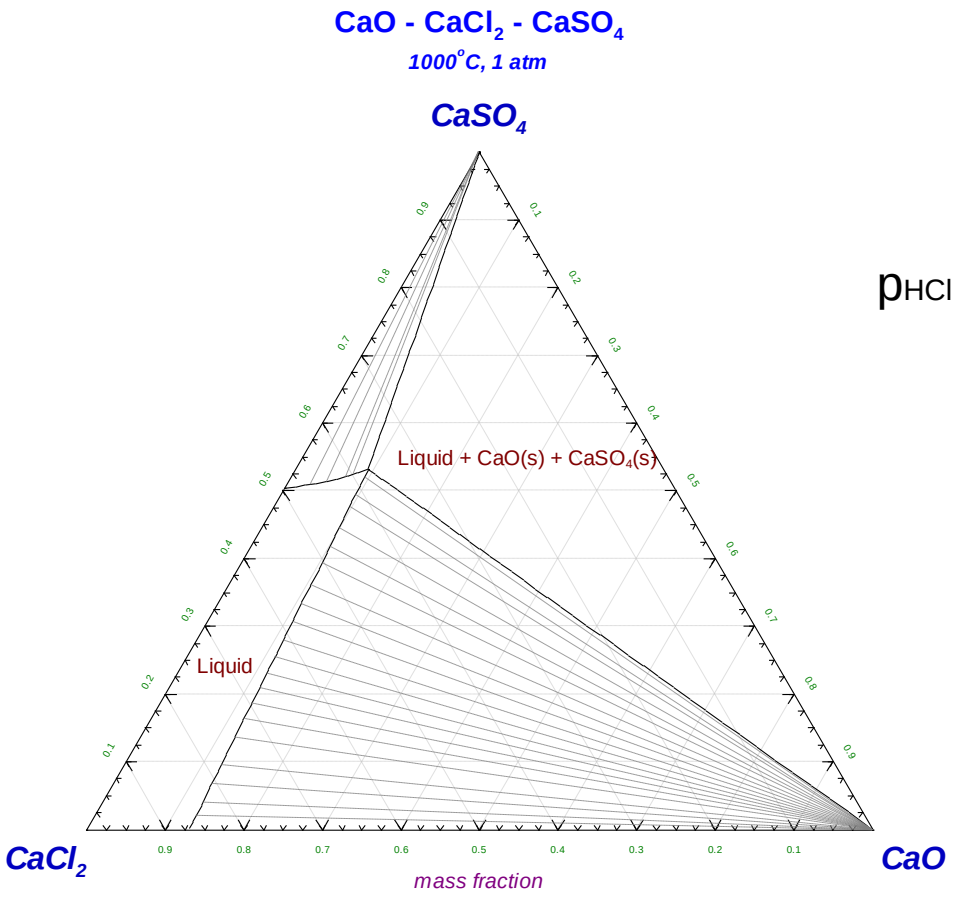
p_{HCl} for KCl-CaO mixture

=

0.014 mbar @ 900°C

Chlorine cycling in a rotary kiln

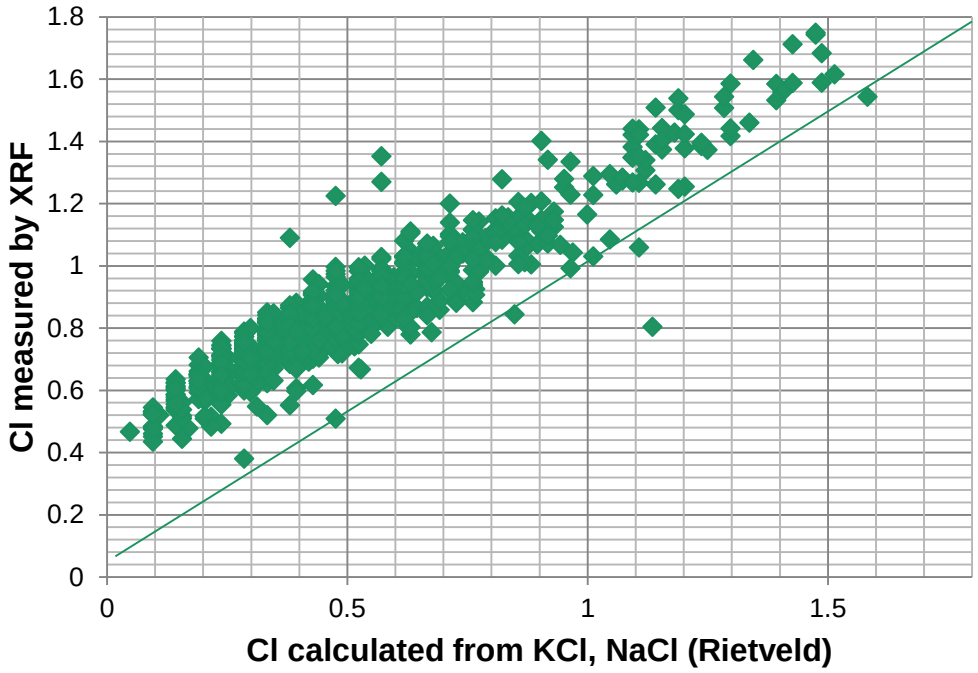
Kiln inlet



p_{HCl} for $CaCl_2$-$CaSO_4$-CaO mixture
=
3.1 mbar @ 900°C

Chlorine cycling in a rotary kiln

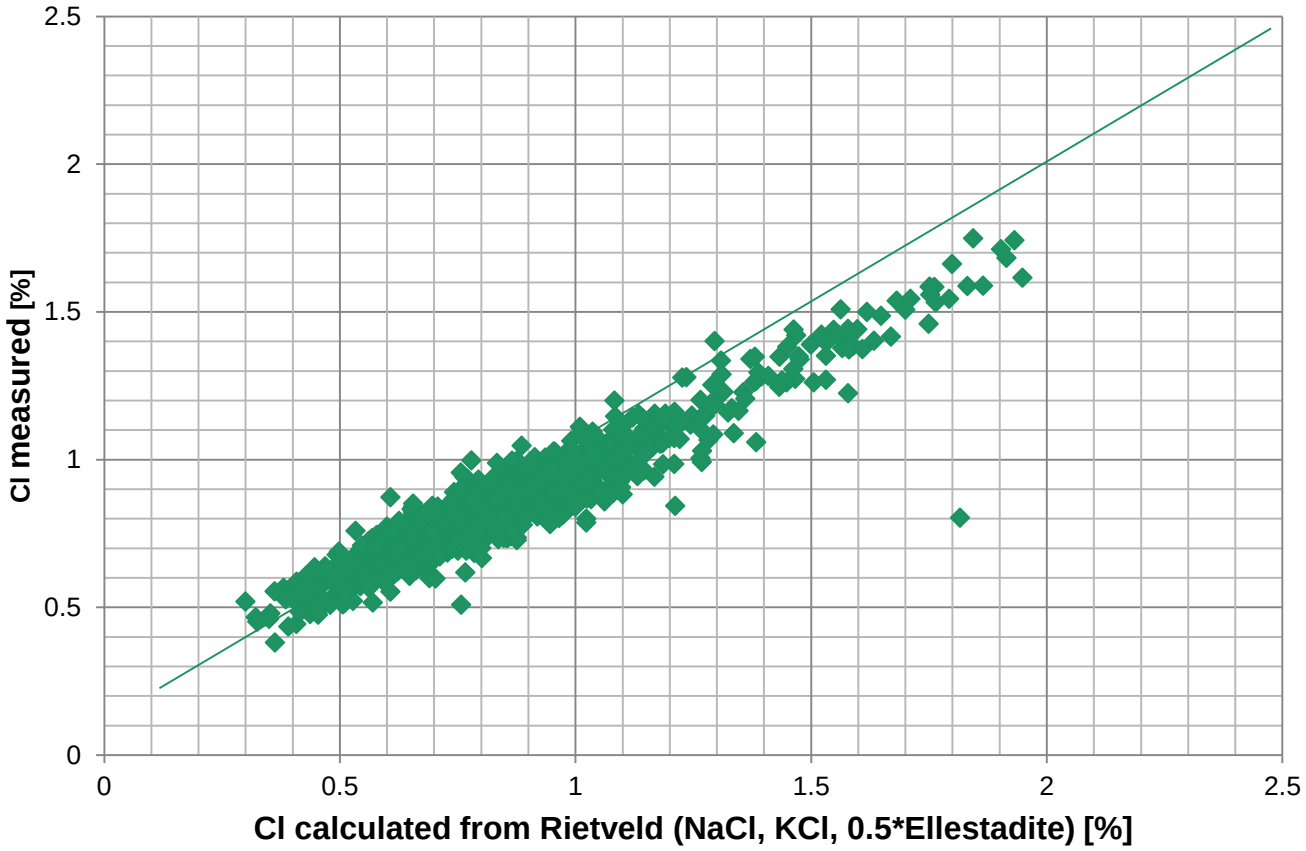
Kiln inlet



- No $CaCl_2$ detected in XRD analyses
- Main contribution from alkali chlorides
- Other Cl-bearing species
  - $Ca_{12}Al_{14}O_{32}Cl_2$
  - $Ca_{10}(SiO_4)_3(SO_4)_3(OH,Cl)I_2$

Chlorine cycling in a rotary kiln

Kiln inlet



Chlorine cycling in a rotary kiln

Kiln inlet

- **Main contribution at kiln inlet are alkali chlorides**
- **All chlorides are liquid initially and form a salt melt**
- **Some CaO can be dissolved if $CaCl_2$ is present**
- **$CaSO_4$ dissolves and increases the amount of liquid phase**
- **$CaCl_2$ and $CaSO_4$ in the salt melt react with Alumina and Silica to form solid compounds (Mayenite, Ellestadite) with high sticking potential**
  - Ring formation + blockages
  - Ball formation

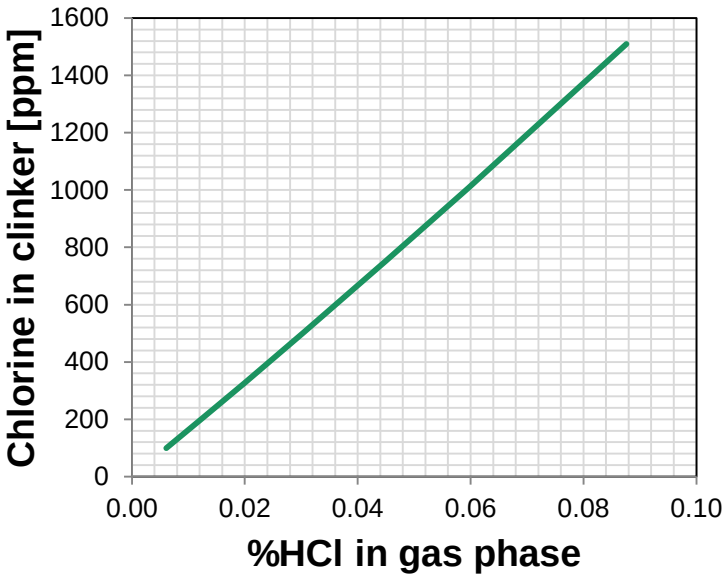
Chlorine cycling in a rotary kiln

Sintering zone

- **Vaporization zone**
- **Limited gas-solid interaction**
- **Congruent vaporization of alkali-chlorides**
  - KCl(l) = KCl(g)
  - The reaction is independent of HCl in the gas
- **Decomposition for other chlorides**
  - $CaCl_2(l) + H_2O(g) = CaO\ (s,l) + 2\ HCl\ (g)$
  - The reaction depends on $H_2O(g)$ and HCl(g) in the combustion gas
- **Typical chlorine levels in clinker : 300 to 1500 ppm (0.03% to 0.15%)**
  - Regulatory level in final cement: 0.1%

Chlorine cycling in a rotary kiln

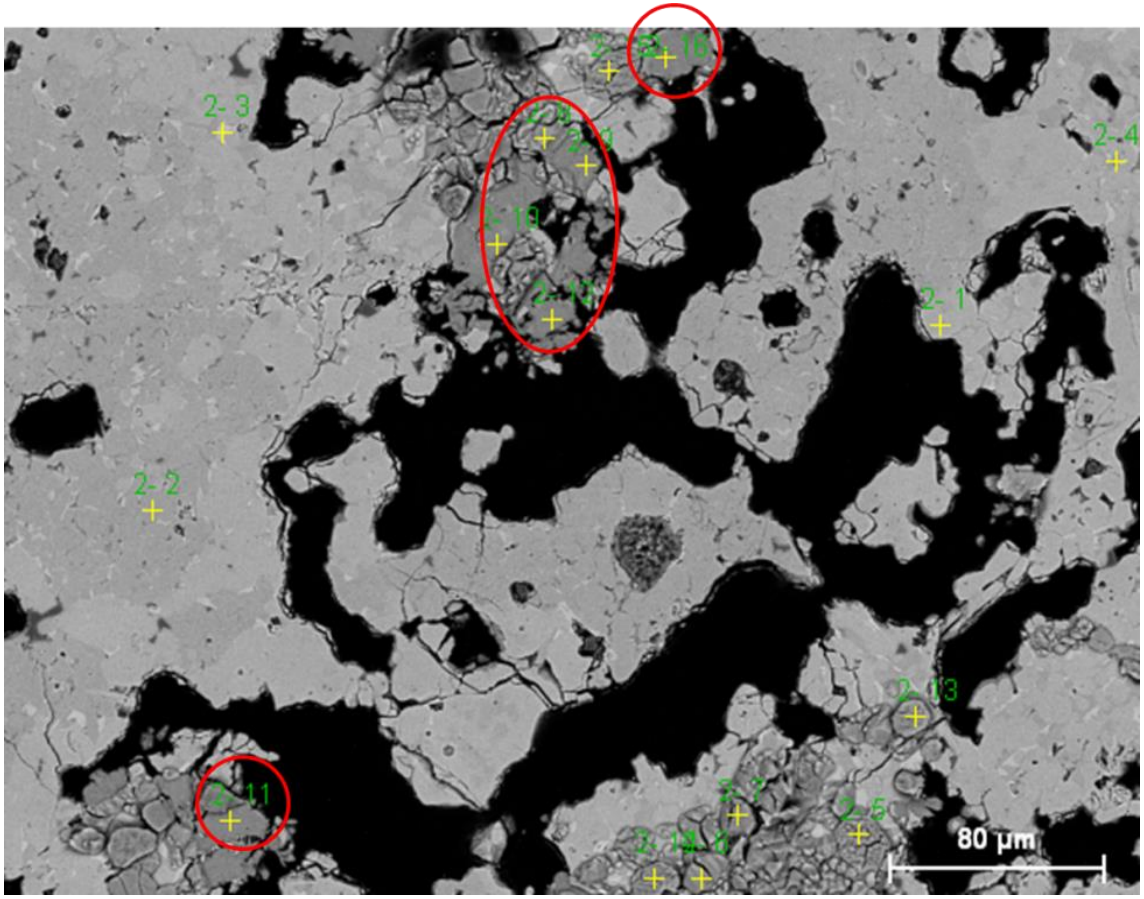
Sintering zone



- Simulation with FTOxid + diluted sulfate / chloride
- Main Cl-bearing species
  - 75% ”$CaCl_2$”
  - 15% “$FeCl_3$”
  - 5% “$MgCl_2$”
  - 4% “KCl”
  - 1% “NaCl”

Chlorine cycling in a rotary kiln

Clinker cooling



- High level of CaO
- 0.19 – 0.54% of Cl
- some K, S

Conclusions

- **There are two different chlorine cycles in a cement kiln**
  - Alkali-chlorides
  - $CaCl_2$ with HCl as vector
- **Chlorides lead to liquid phase formation with high sticking potential at kiln inlet**
- **The alkali chlorides accumulate in the kiln if no by-pass is present**
- **Some chlorine leaves with the clinker (up to 0.15%), mainly as $CaCl_2$**
- **It is difficult to simulate chlorine cycling**
  - Missing thermodynamic data
  - Highly process dependant : residence time (inclination, bed height, rotation speed), kiln geometry, temperature profile