معهد المستقبل العالي للهندسة بالفيوم

FUTURE HIGH INSTITUTE OF ENGINEERING IN FAYOUM

Cement Chemistry

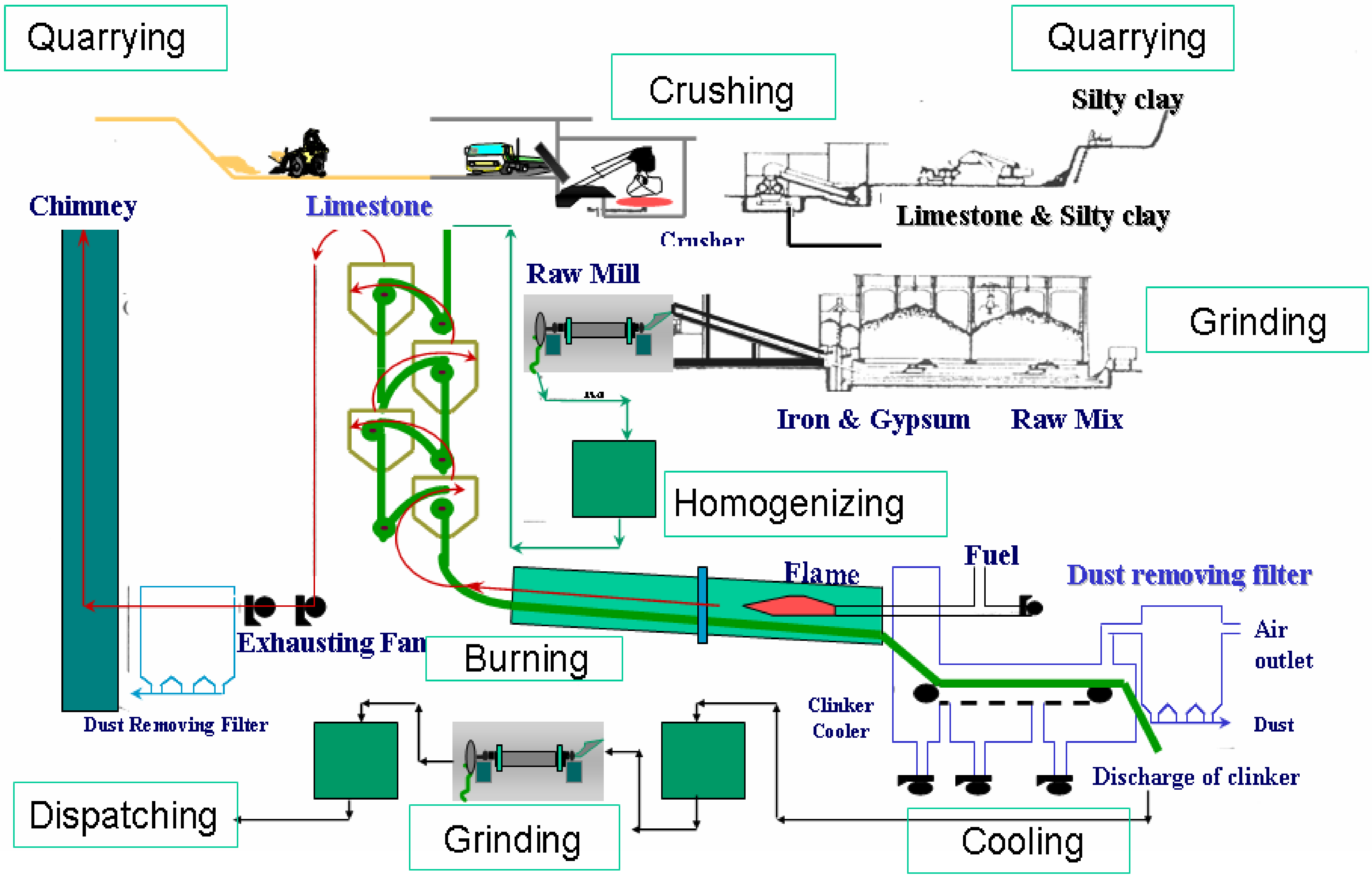
DR- Abdelrahman Ragab

Cement Definition

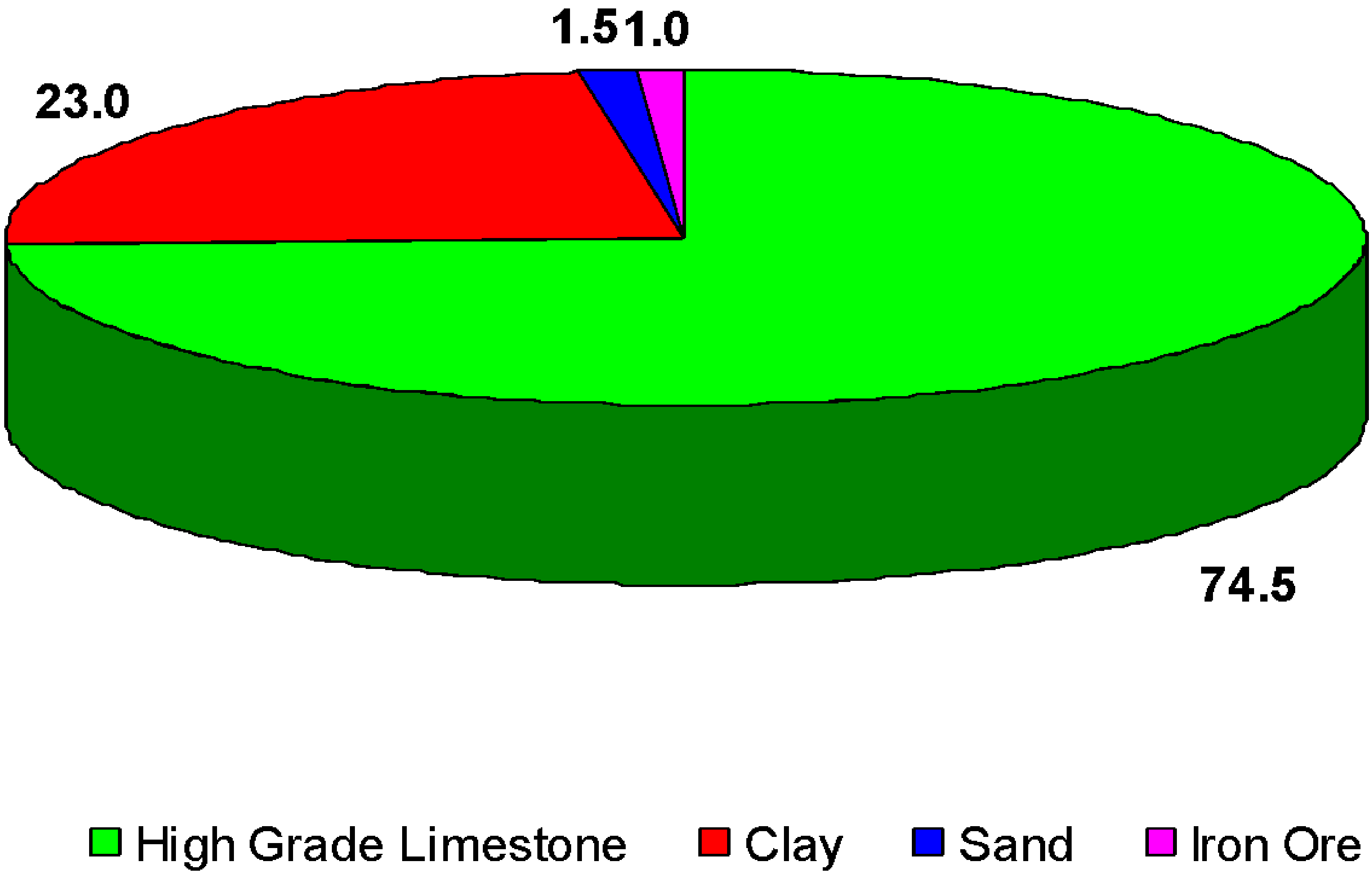
Is defined as the product obtained from Limestone and Clay raw materials burned at temperature 1450 C and grinding the resulting clinker

Corrective Materials

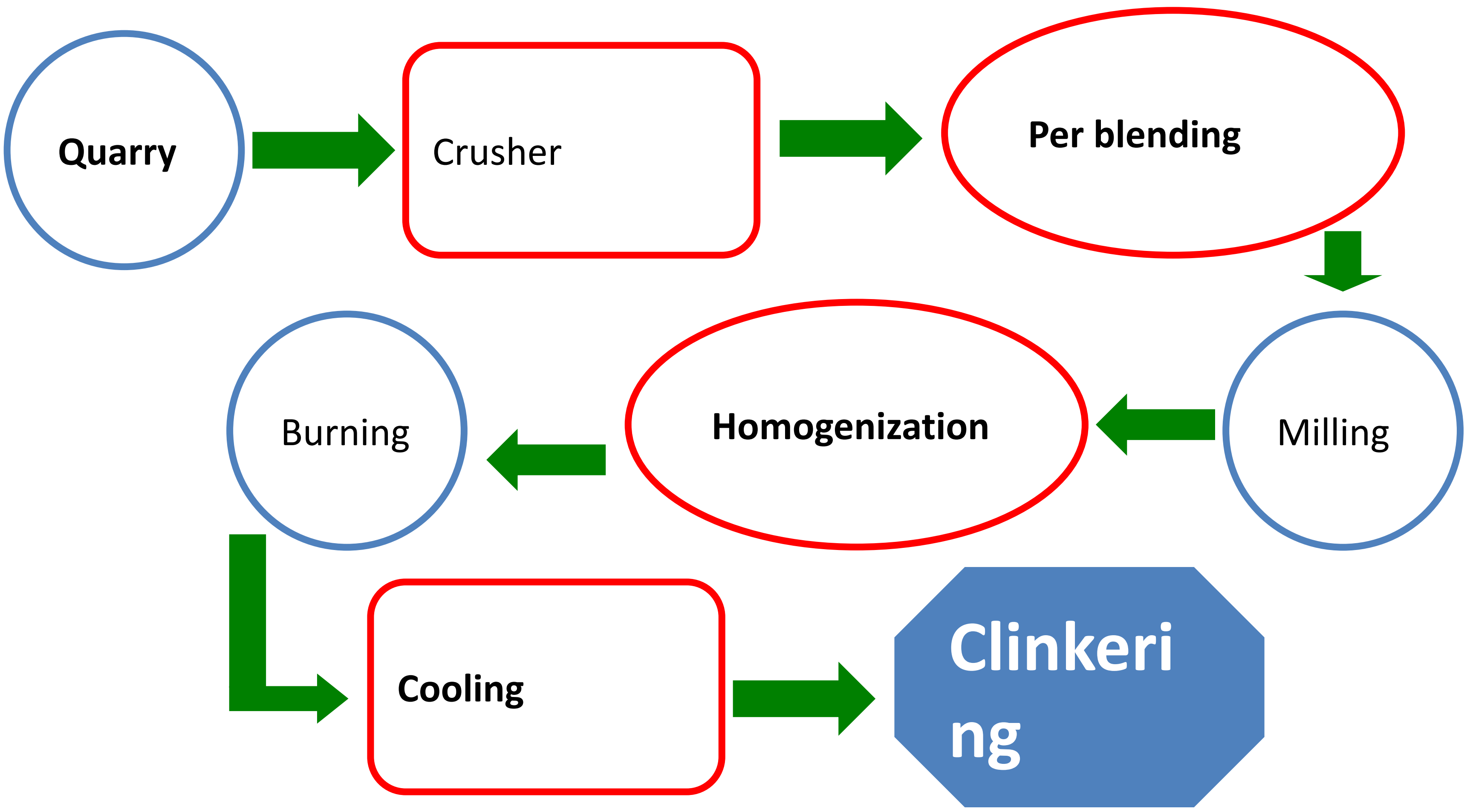
- Iron Ore
- Silica Sand
- Bauxite



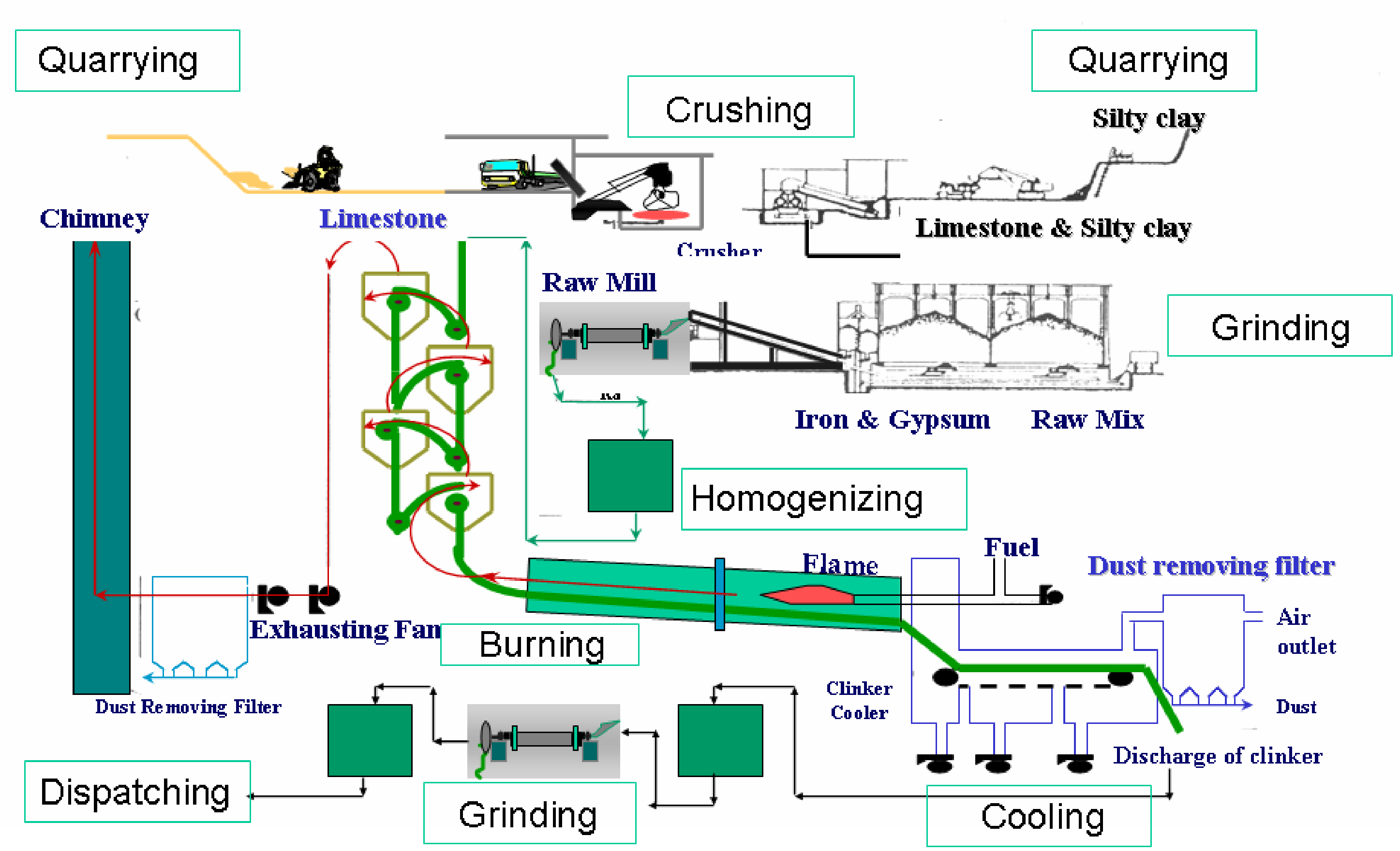
Quarrying
Crushing
Quarrying
Silty clay
Chimney
Limestone
Crusher
Limestone & Silty clay
Raw Mill
Grinding
Iron & Gypsum
Raw Mix
Homogenizing
Fuel
Flame
Dust removing filter
Exhausting Fan
Burning
Air
outlet
Dust Removing Filter
Clinker
Cooler
Dust
Discharge of clinker
Dispatching
Grinding
Cooling


1.5
1.0
23.0
74.5
High Grade Limestone
Clay
Sand
Iron Ore

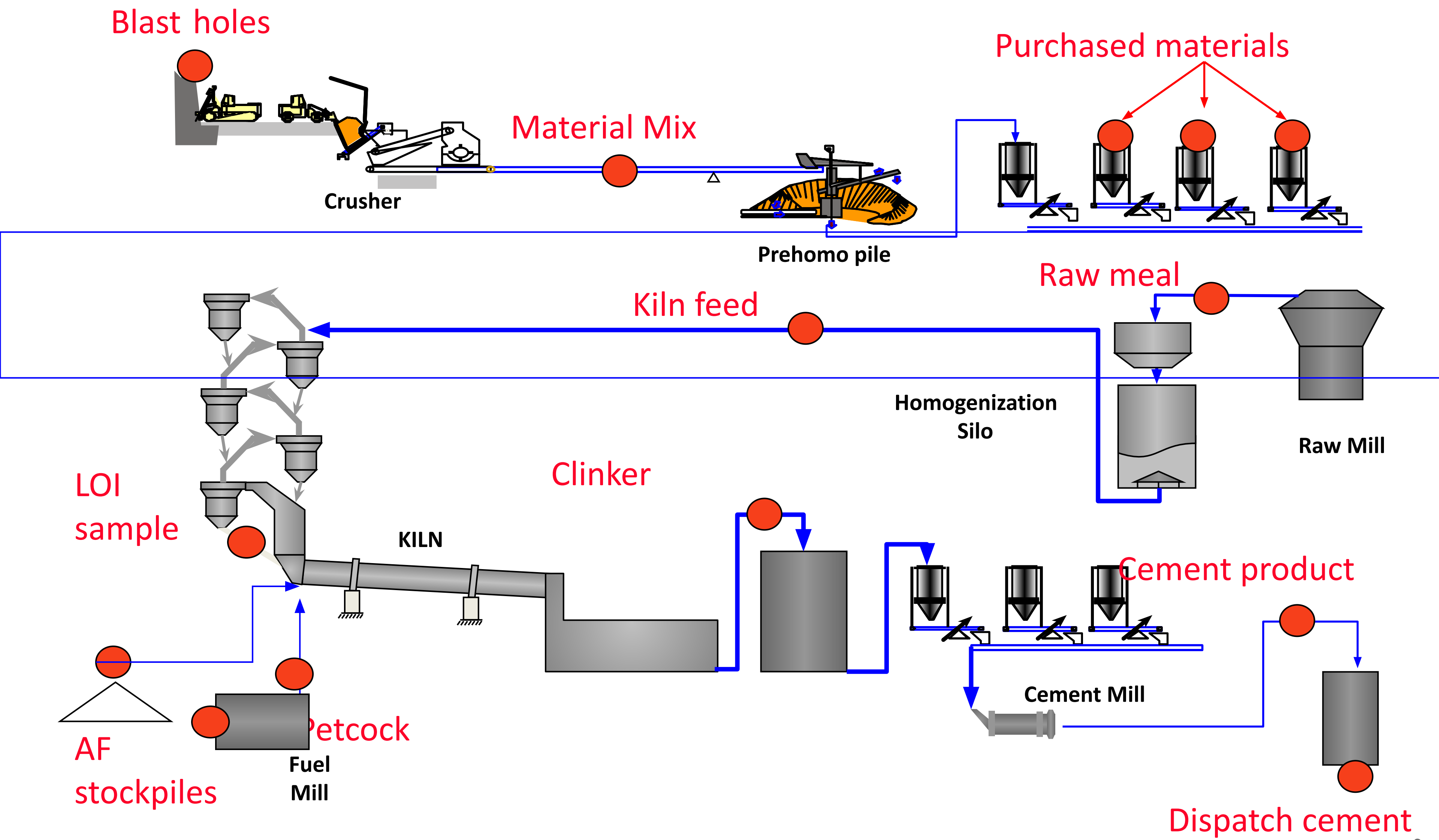
Stages of Clinker Manufacturing



Stages of Clinker Manufacturing



Process Flow and Sampling points



Clinker Process Formation

Production Steps

- Zone 1: dehydration
- Zone 2: chemical reactions
- Zone 3: clinkering
- Zone 4: cooling

Clinker Process Formation

Zone 1 - Dehydration

- about 100°C:

  Free water evaporation

  - Dry process: 1-3%

- 350-600°C:

  clays dehydration

  ? high reactive component

Clinker Process Formation

Zone 2 - Decarbonation

- 600-800°C:

  $MgCO_3 \rightarrow MgO + CO_2$

- 800-1050°C:

  $CaCO_3 \rightarrow CaO + CO_2$

- From 700°C,

  Formation of alkaline sulfates (Na_2O, K_2O, $CaO – SO_3$)

Clinker Process Formation

Zone 3 - Clinkering

- > 800°C

  - Iron oxide combines with alumina & lime to form C_4AF

  - Then, the remaining alumina will react with lime to form C_3A

  - Silica and lime start to form C_2S

- > 1200°C

  - Formation of C_3S (C_2S reacts with remaining lime)

- > 1338°C:

  C_4AF and C_3A generate the liquid phase

  - accelerates solid/solid chemical reactions (silica/ lime)
  - contributes to burnability

Clinker Process Formation

Zone 4 - Cooling

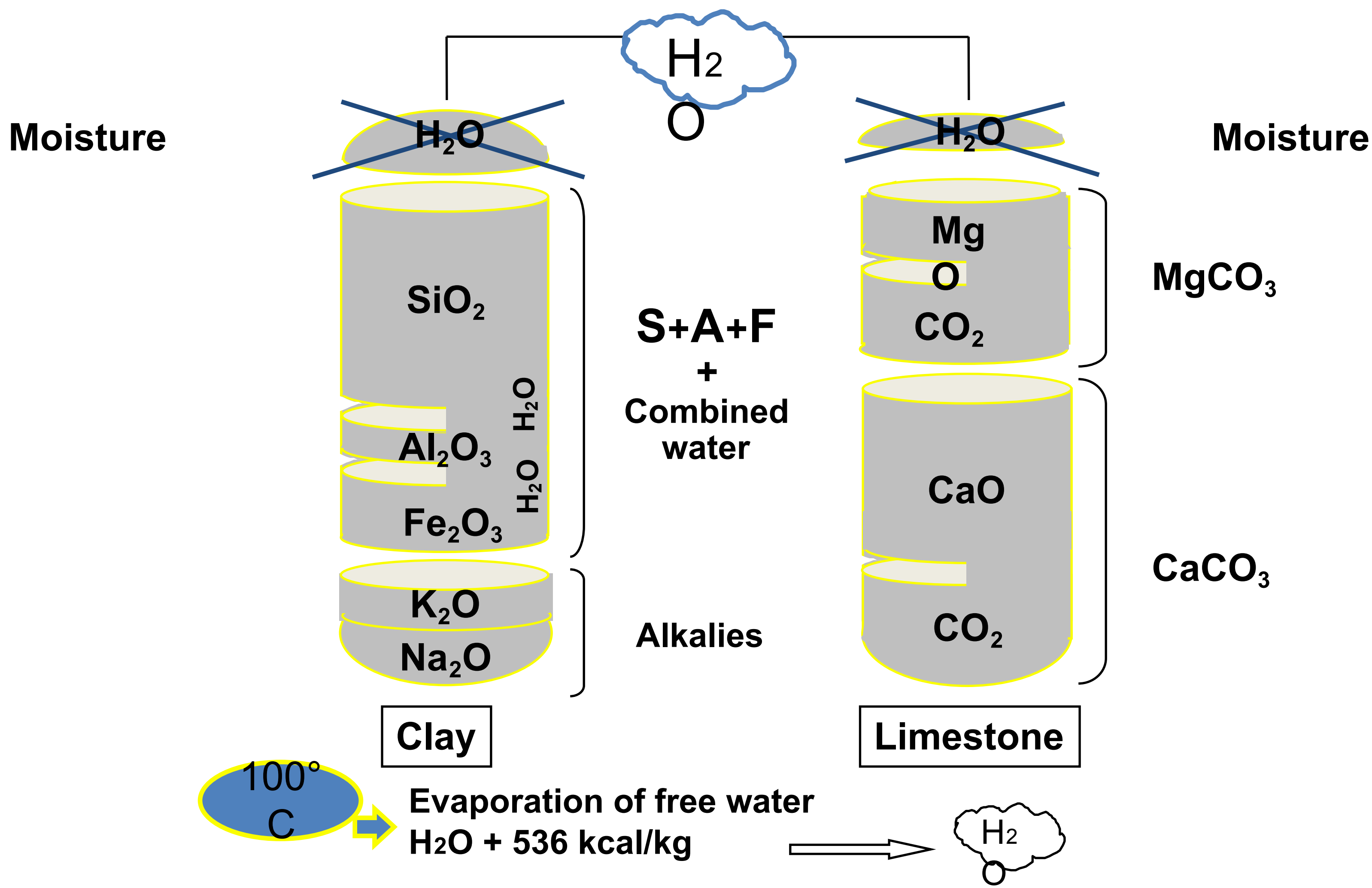
- Precipitate the liquid phase small reactive crystals
- MgO < 2%, magnesia gets into silicate and aluminate crystal networks

  (MgO> 2% periclase formation)

- Quenching to set clinker reactions:
  - prevent C_3S reversion to C_2S γ + C
  - prevent C_2S transformation into non-hydraulic C_2S γ (powdery)
  - smaller MgO periclase crystals

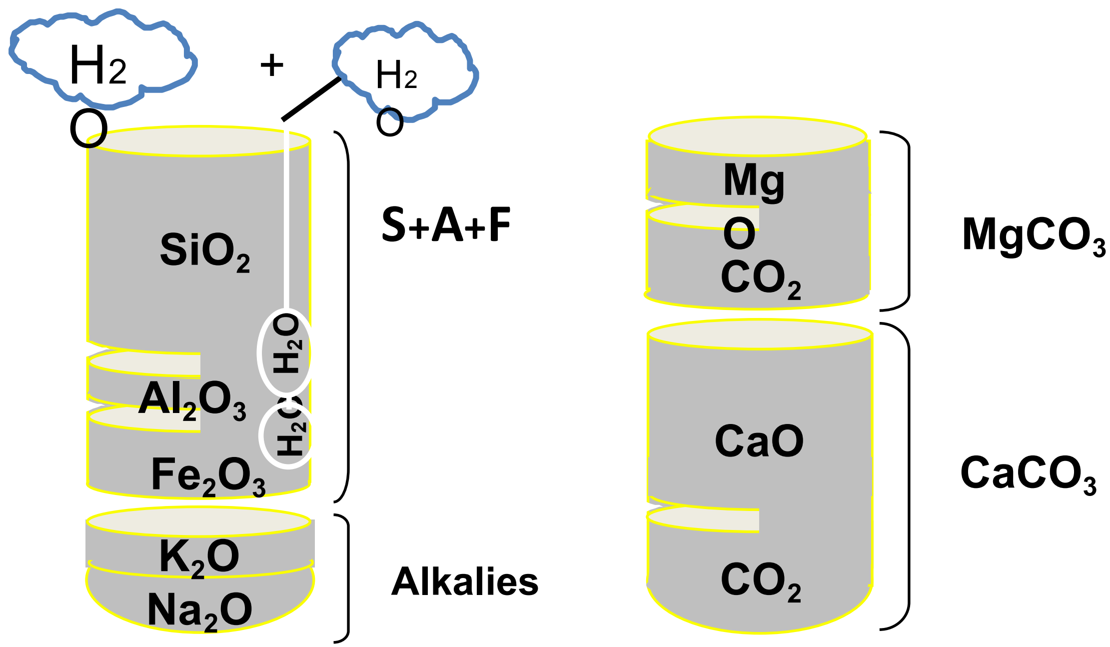
Chemical Reactions

1st stage: evaporation



Chemical Reactions

2nd stage: dehydration



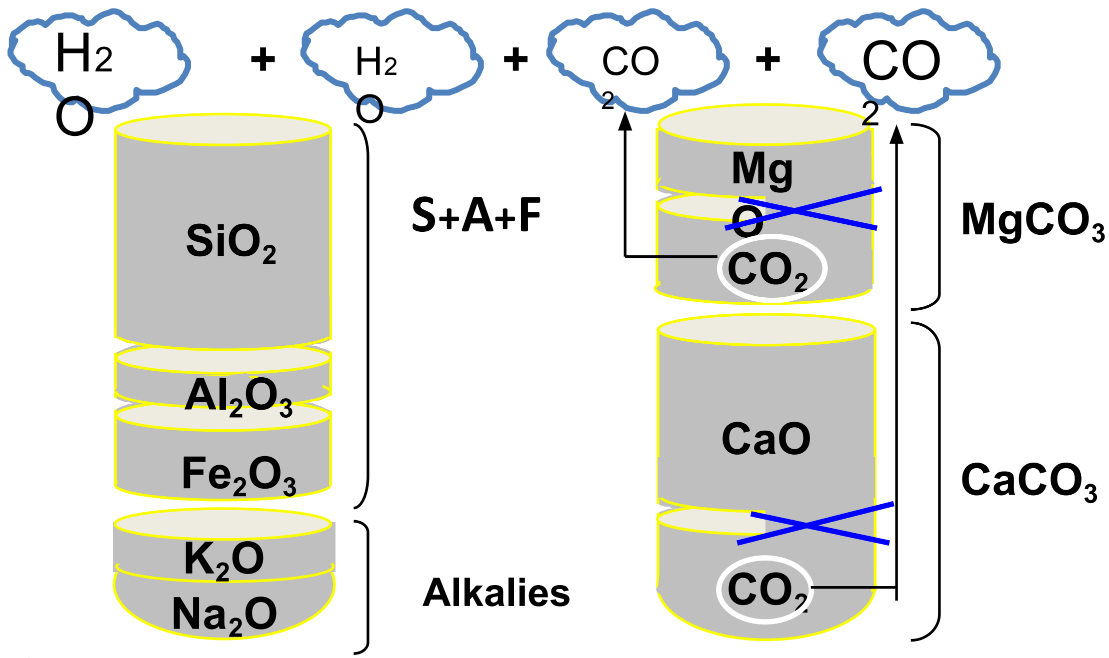
250° C
to
450° C

The combined water of clay goes away

H_2O + 20 kcal/kg rawmix → H_2O

Chemical Reactions

3rd stage: decarbonation

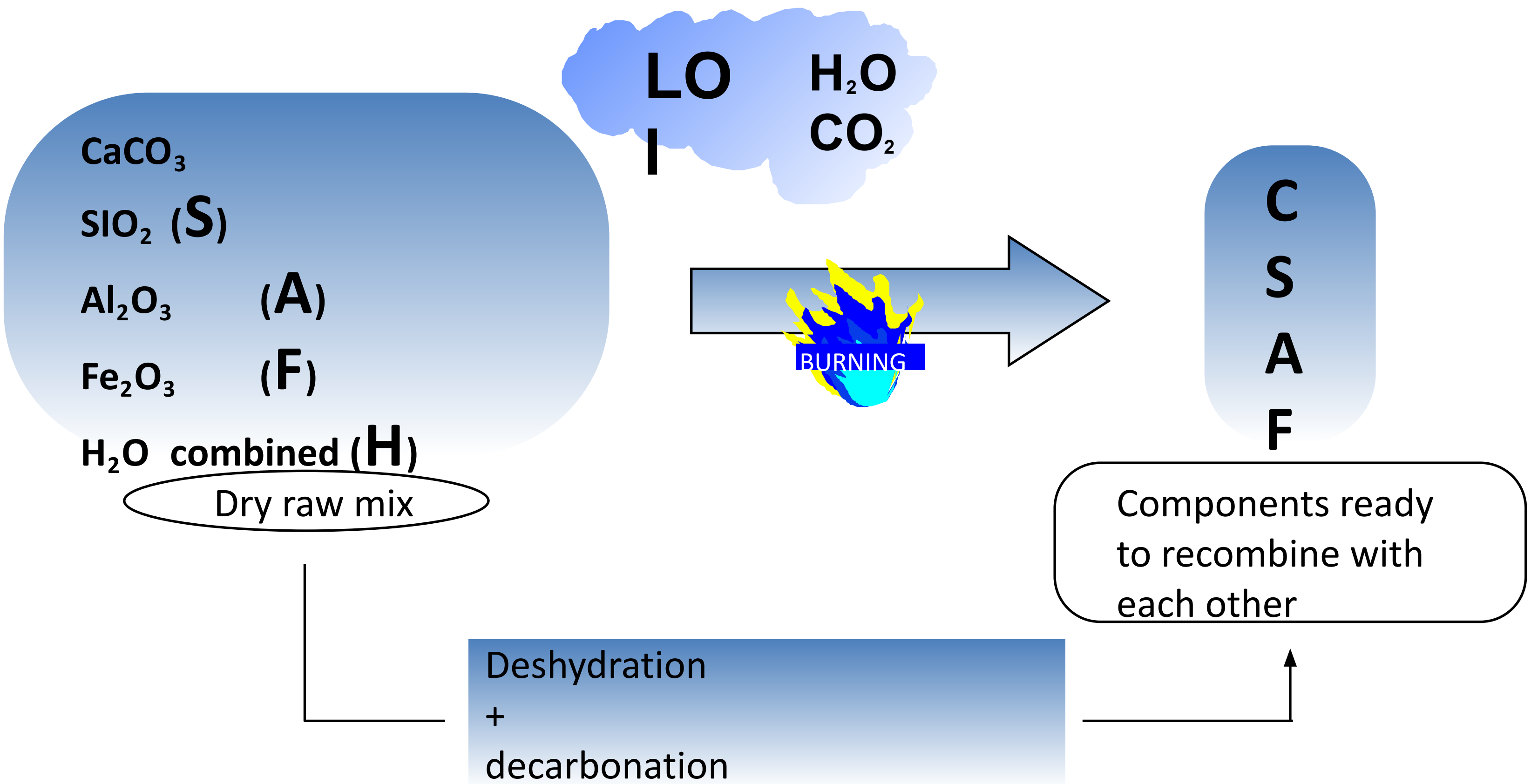


450 to 650/700 °C ➡ $MgCO_3$ + 310 kcal/kg de $MgCO_3$ ➡ MgO + CO_2 L.O.I.

820 to 950 °C ➡ $CaCO_3$ + 423 kcal/kg de $CaCO_3$ ➡ CaO + CO_2 L.O.I.

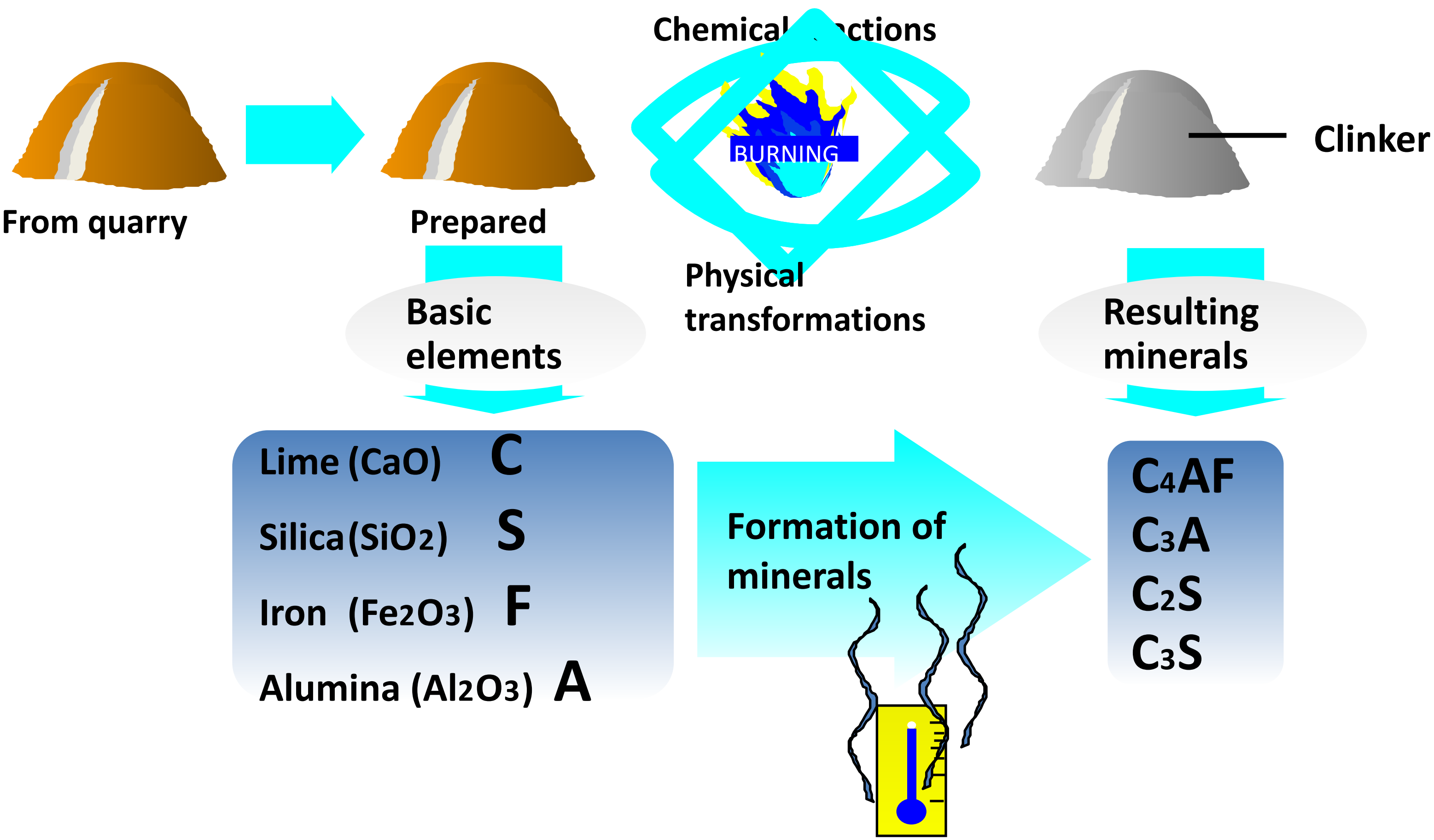
Chemical Reactions

Loss of ignition



Chemical Reaction

4th stage: clinkerisation

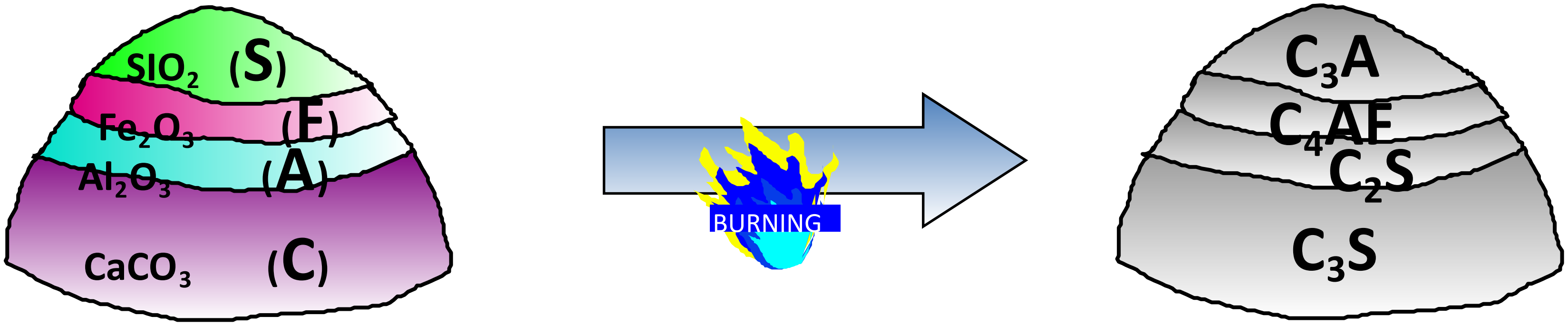


Chemical Reactions

4th stage: clinkerisation

Decarbonated raw mix
An inert product

Clinker
A hydraulic binder
An active product



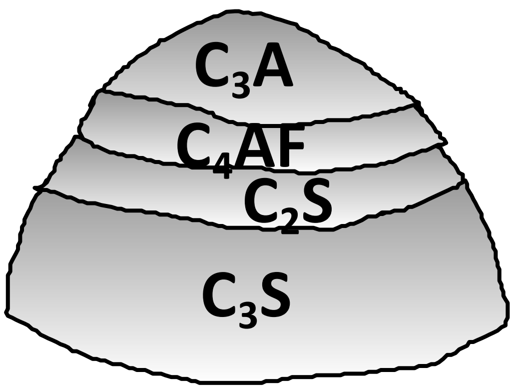
Clinkerization

- **Appearance of the liquid phase**
- **Formation of C_2S and C_3S**

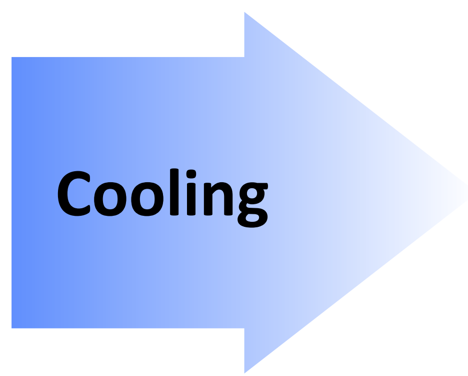
Chemical Reactions

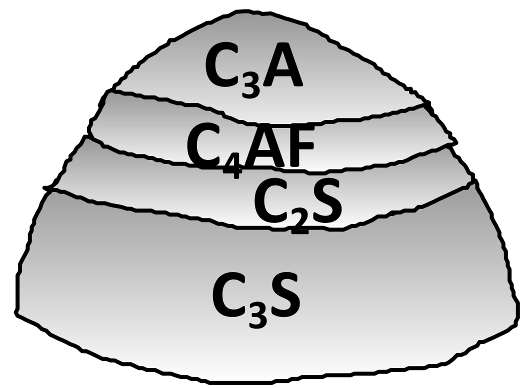
5th stage: cooling

Why?
- **To transport**
- **Quenching**
- **To save energy**



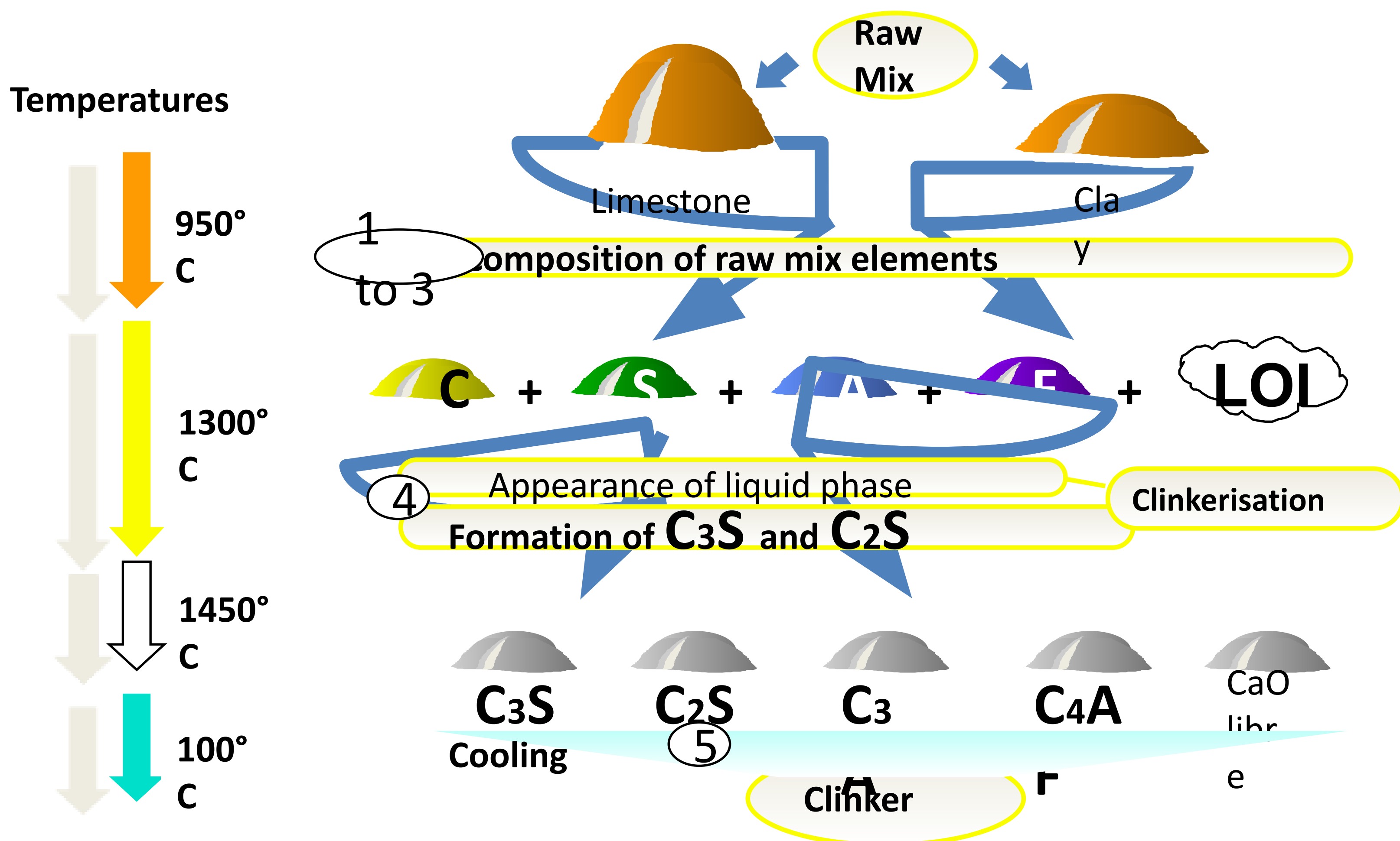
At 1500° C





At 150° C

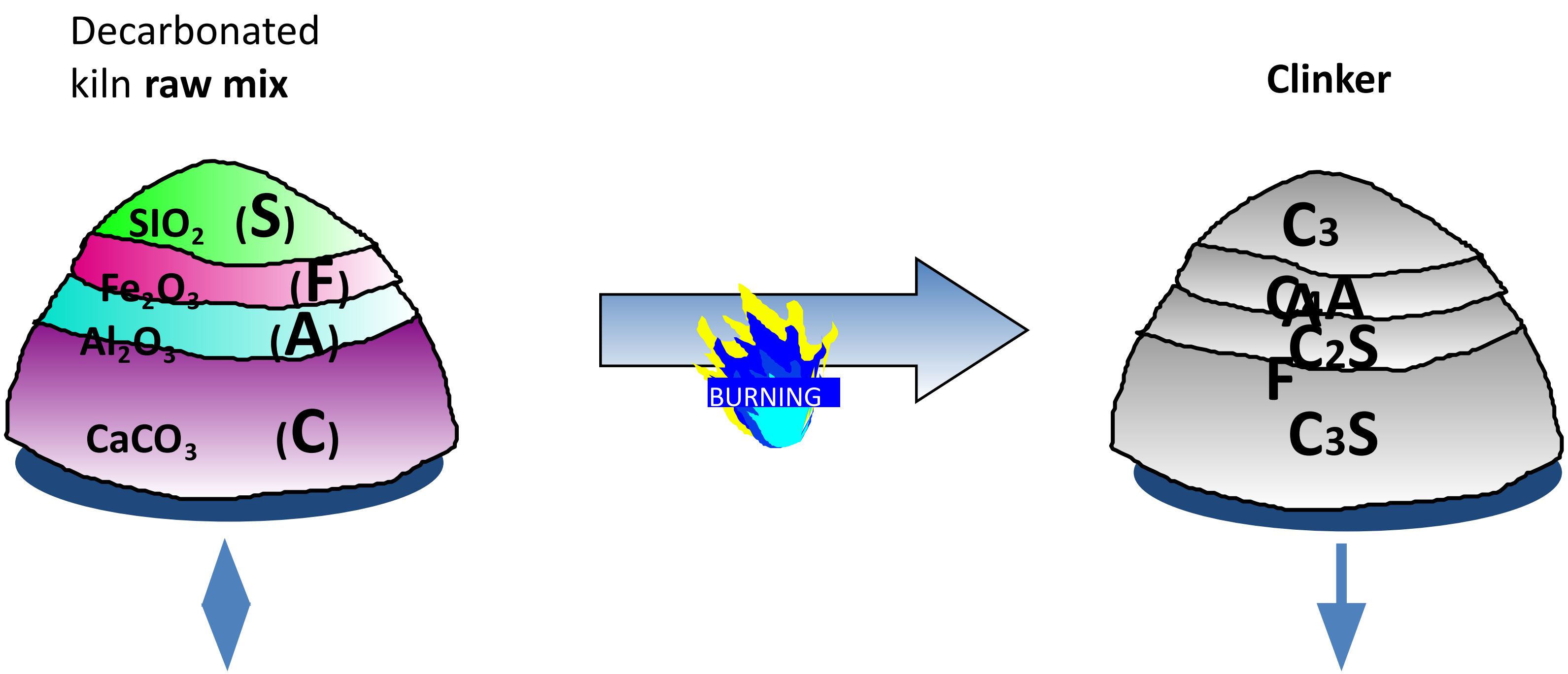
From raw mix to clinker…



Clinker Minerals

SHORT SYMBOL	CHEMICAL FORMULA	NAME	%
C3S	$(CaO)_3\ SiO_2$	Tricalcium silicate or alite	50 to 70%
C2S	$(CaO)_2\ SiO_2$	Bicalcium silicate or belite	10 to 20%
C3A	$(CaO)_3\ Al_2O_3$	Tricalcium aluminate or celite	1 to 15 %
C4AF	$(CaO)_4\ Al_2O_3\ Fe_2O_3$	Tetracalcium aluminoferrite or felite	0 to 15 %

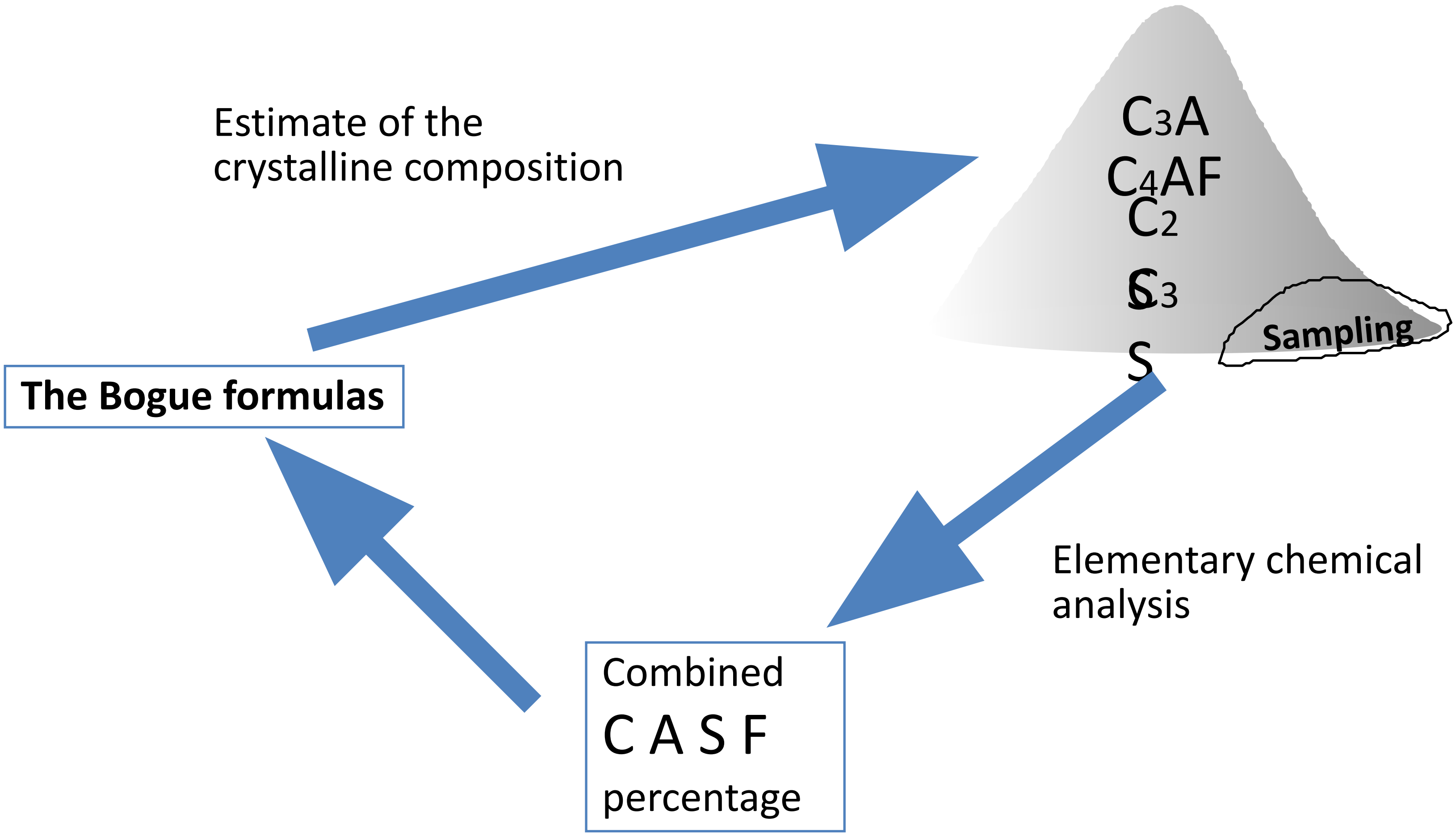
Clinker Minerals



Any changes in the 4 raw mix elements will change the proportions of the 4 clinker minerals, and thus the clinker quality

The type of clinker required determines what the proportions of the 4 minerals should be

Clinker Minerals



Clinker Minerals

Bogue Equations

Try to find the 1st Bogue formulae, giving the quantity of

1 mole Fe_2O_3 → ...le C_4AF

→ Fe_2O_3

→ Al_2O_3

→ Ca O

160 g ← 486 g

Fe = 56 g
O = 16 g
C = 12 g
Ca = 40 g
Al = 27 g

i.e. $C_4AF = 3{,}04\ F$

Clinker Minerals

Bogue Equations

$$C_4AF = 3{,}04\ \mathbf{F}$$

$$C_3A = 2{,}65\ \mathbf{A} - 1{,}69\ \mathbf{F}$$

$$C_2S = 8{,}60\ \mathbf{S} + 1{,}08\ \mathbf{F} + 5{,}07\ \mathbf{A} - 3{,}07\ \mathbf{C}$$

$$C_3S = 4{,}07\ \mathbf{C} - 7{,}60\ \mathbf{S} - 1{,}43\ \mathbf{F} - 6{,}72\ \mathbf{A}$$

with

$$\mathbf{C} = CaO - fCaO - 0.7SO_3$$

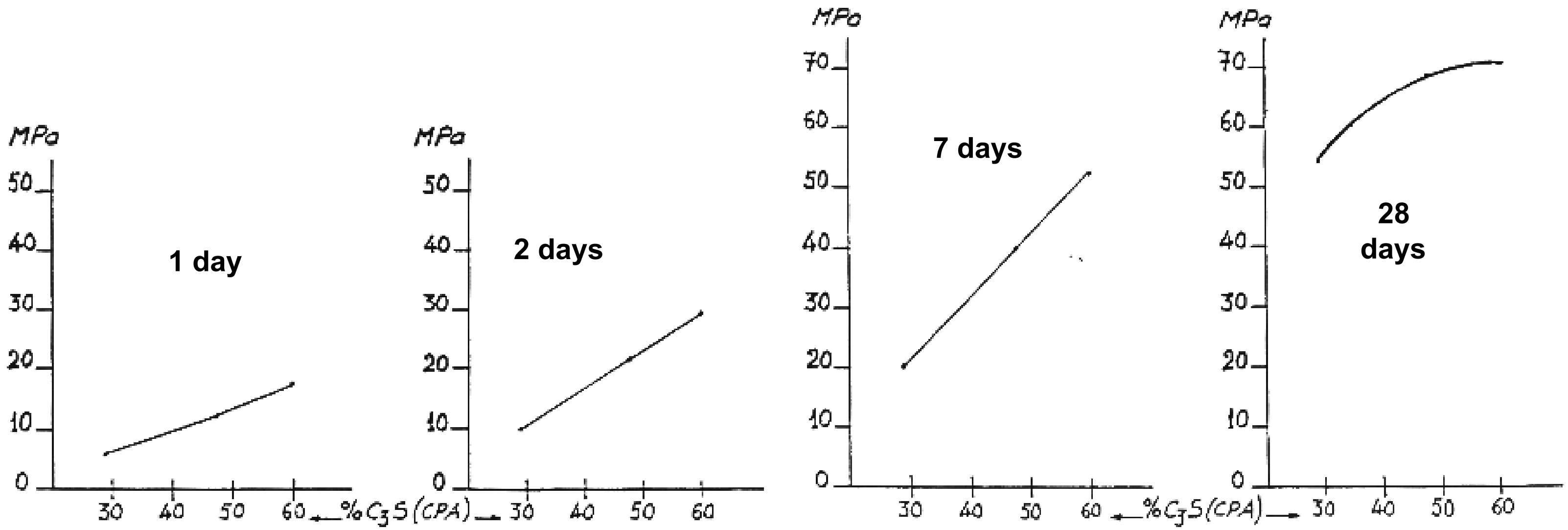
Clinker Minerals

C_3S (Alite)

- Final and initial strengths
- Rapid hydration
- Contains impurities: Mg, Al, Fe
- Typically 50 to 66% of clinker (opt. 62 - 65)
- Difficult to burn if C_3S > 65%
- Ring problems if C_3S is too low

Clinker Minerals

Influence of C_3S on compressive strength



Clinker Minerals

C_2S (Belite)

- Low early strength but good final strength
- Slow hydration
- Contains impurities: alkalis, Al, Fe, fluorides
- Typically 20 to 24% of clinker
- Clinker grindability adversely impacted by higher C_2S
- Important effects on the clinker grindability

Clinker Minerals

C_3A

- Rapid hydration
  - gypsum added to control rate
- Early strengths
- Typically 8 to 15% of clinker
- Important effects on concrete quality and durability
  - workability
  - resistance to sulfates

Clinker Minerals

C_4AF

- Very slow hydration
- No strengths
- Typically 0.5 to 10% of clinker

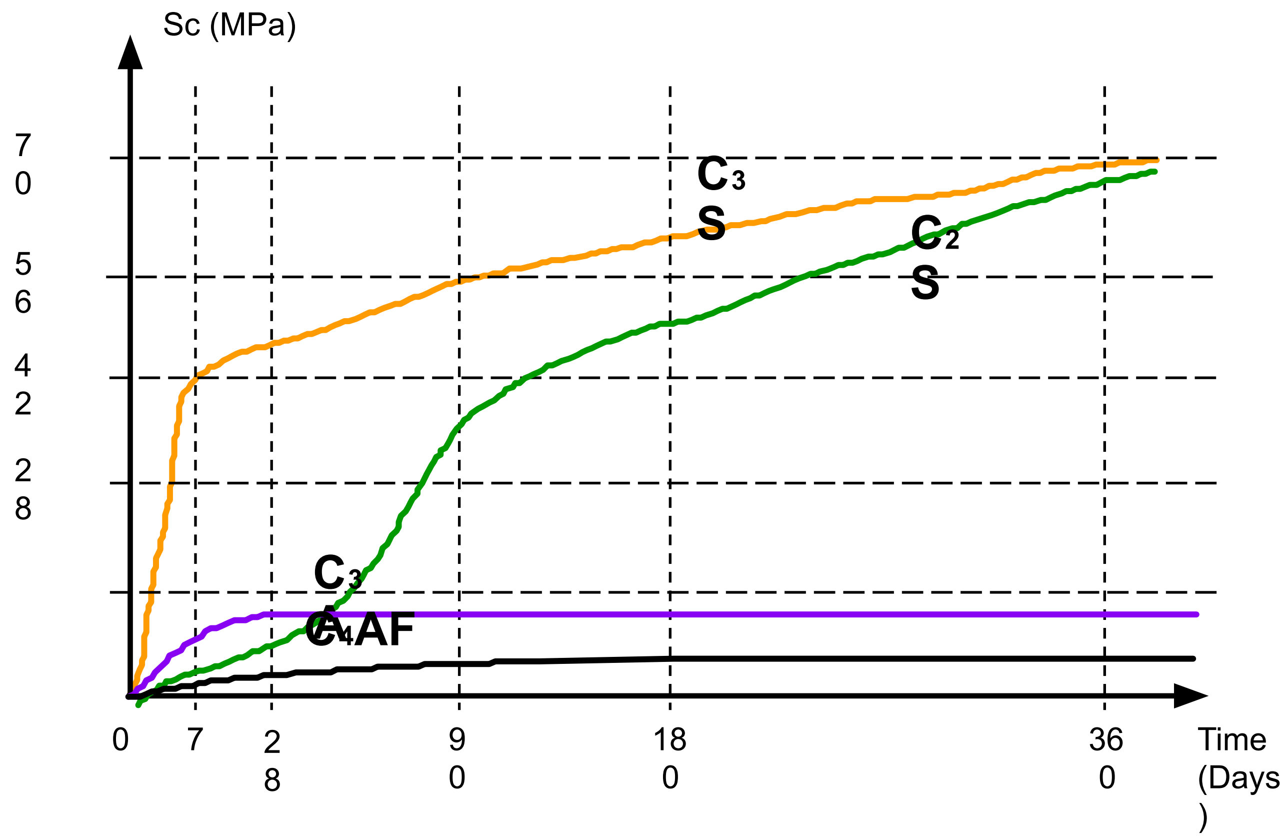
Cement color

more C_4AF = darker cement

Clinker Minerals

Compressive strength

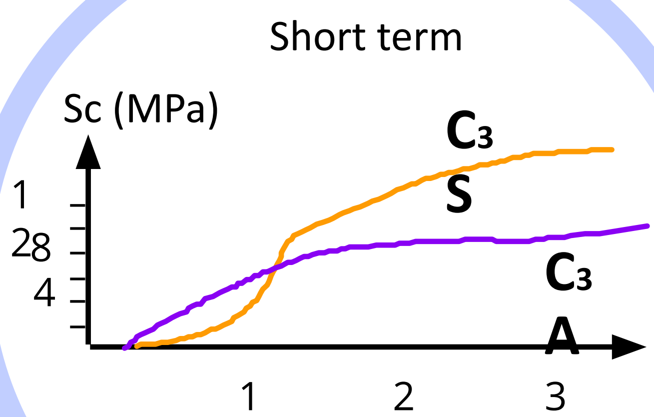
§ Evolution of the clinker compressive strength



Clinker Minerals

C_3A and flash setting

His hydration needs to be controlled



It's very reactive with water

$C_3A + C + nH \longrightarrow C_4AH_{11\text{ to }15}$

Significance of Clinker Minerals for ASTM Cement Types

- Type I Portland no restrictions regarding clinker minerals
- Type II Portland with moderate sulphate resistance (and moderate heat of hydration)

  C_3A max. 8 %

  (C_3S + C_3A max. 58% for moderate heat of hydration)
- Type III Portland with high early strength

  C_3A max. 15% (C_3A max. 8% for moderate sulphate resist. C_3A max. 5% for high sulphate resist.)

Significance of Clinker Minerals for ASTM Cement Types

- Type IV Portland with low heat of hydration

  C_3S max. 35%
  C_2S min. 40%
  C_3A max. 7%

- Type V Portland with high sulphate resistance

  C_3A max. 5.0 %

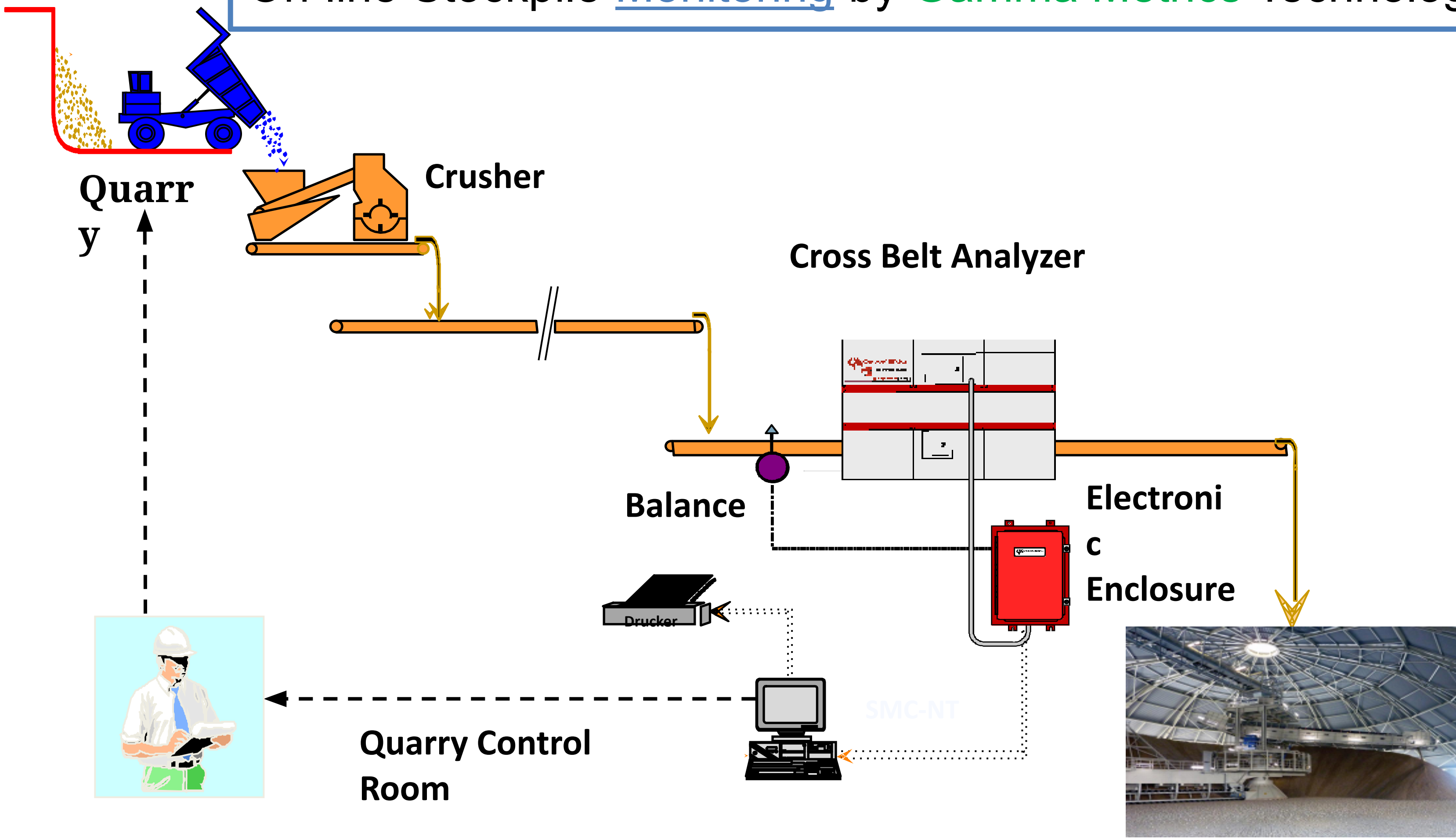
  C_4AF + 2 C_3A max. 25%

  or C_4AF + 2 C_2F max. 25%

Quality Control

Raw Mix Stockpile

On-line Stockpile Monitoring by Gamma Metrics Technology



Thanks