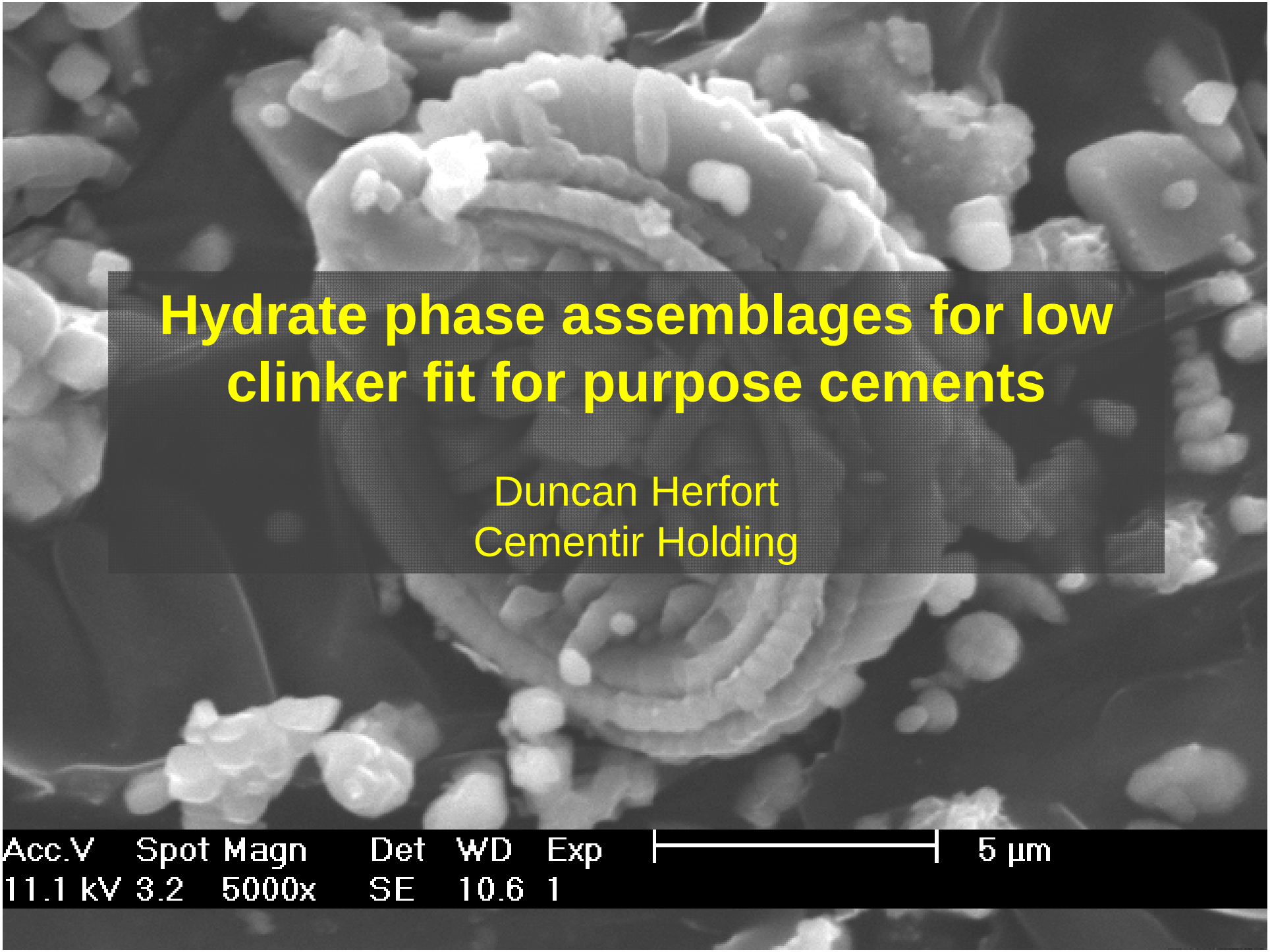


Hydrate phase assemblages for low clinker fit for purpose cements

Duncan Herfort
Cementir Holding

Introduction

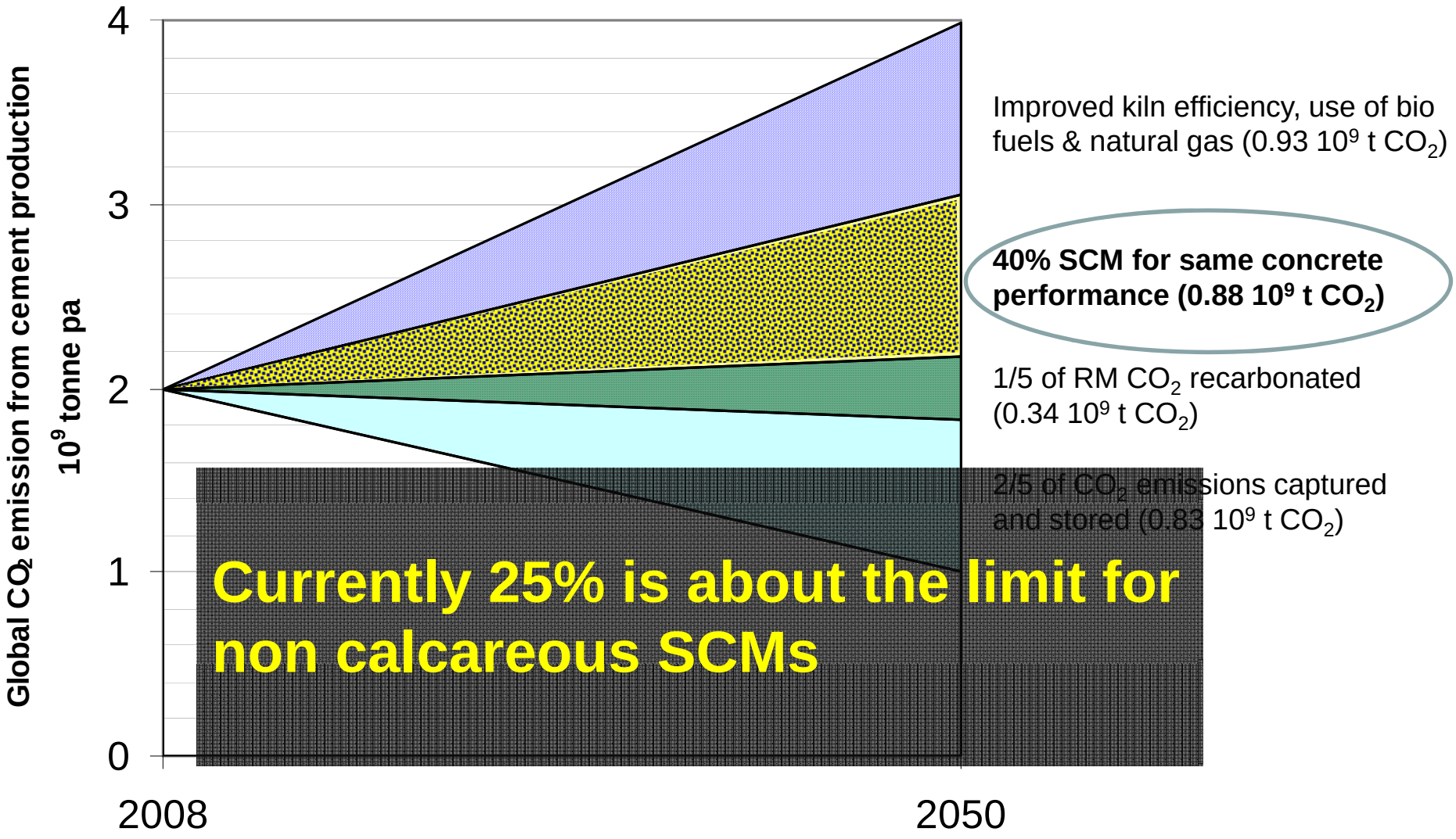
Can we replace 50% clinker by a non-calcareous pozzolana (e.g. class F FA) for same concrete performance?

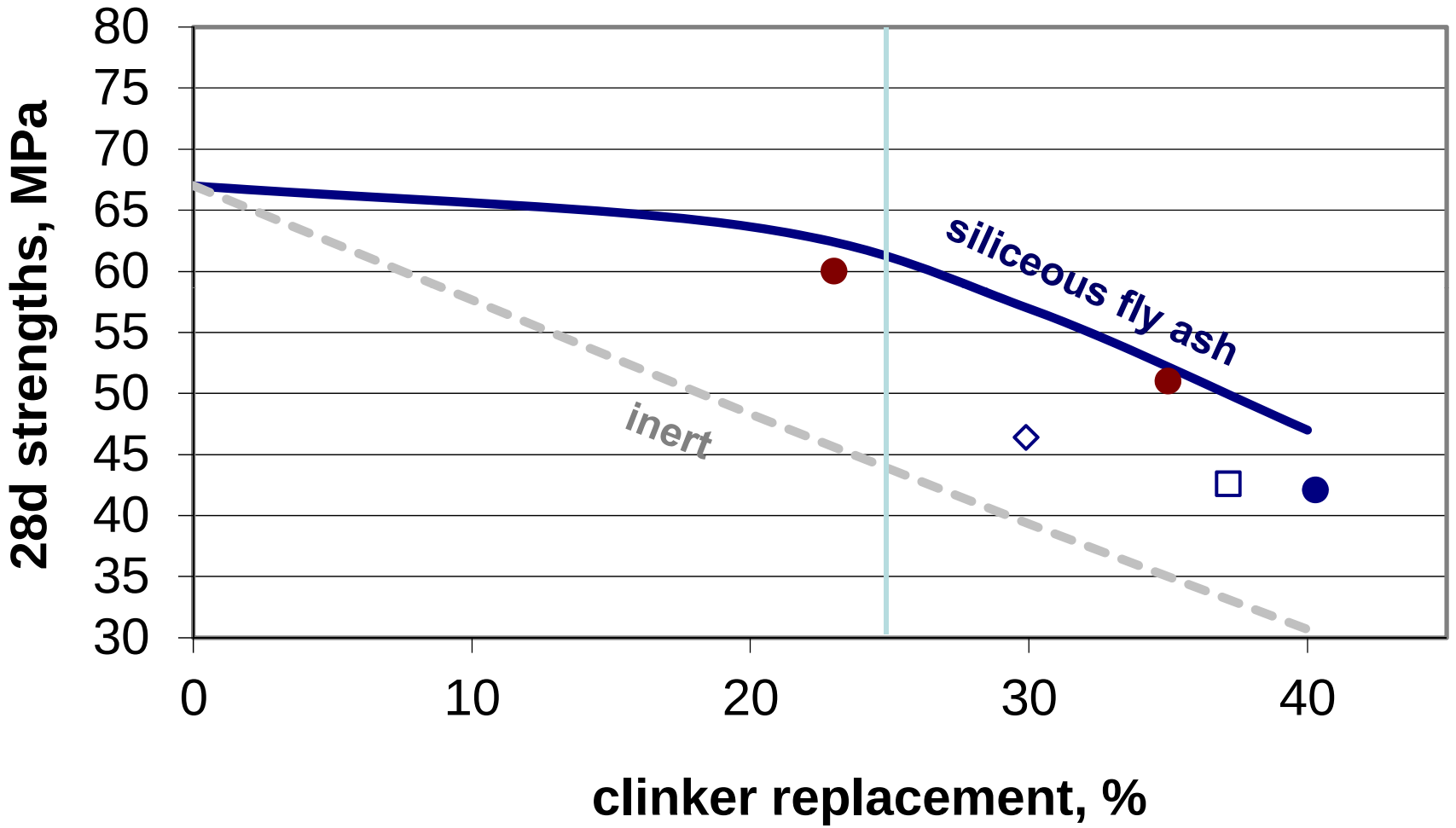
At first glance the answer is no, because the

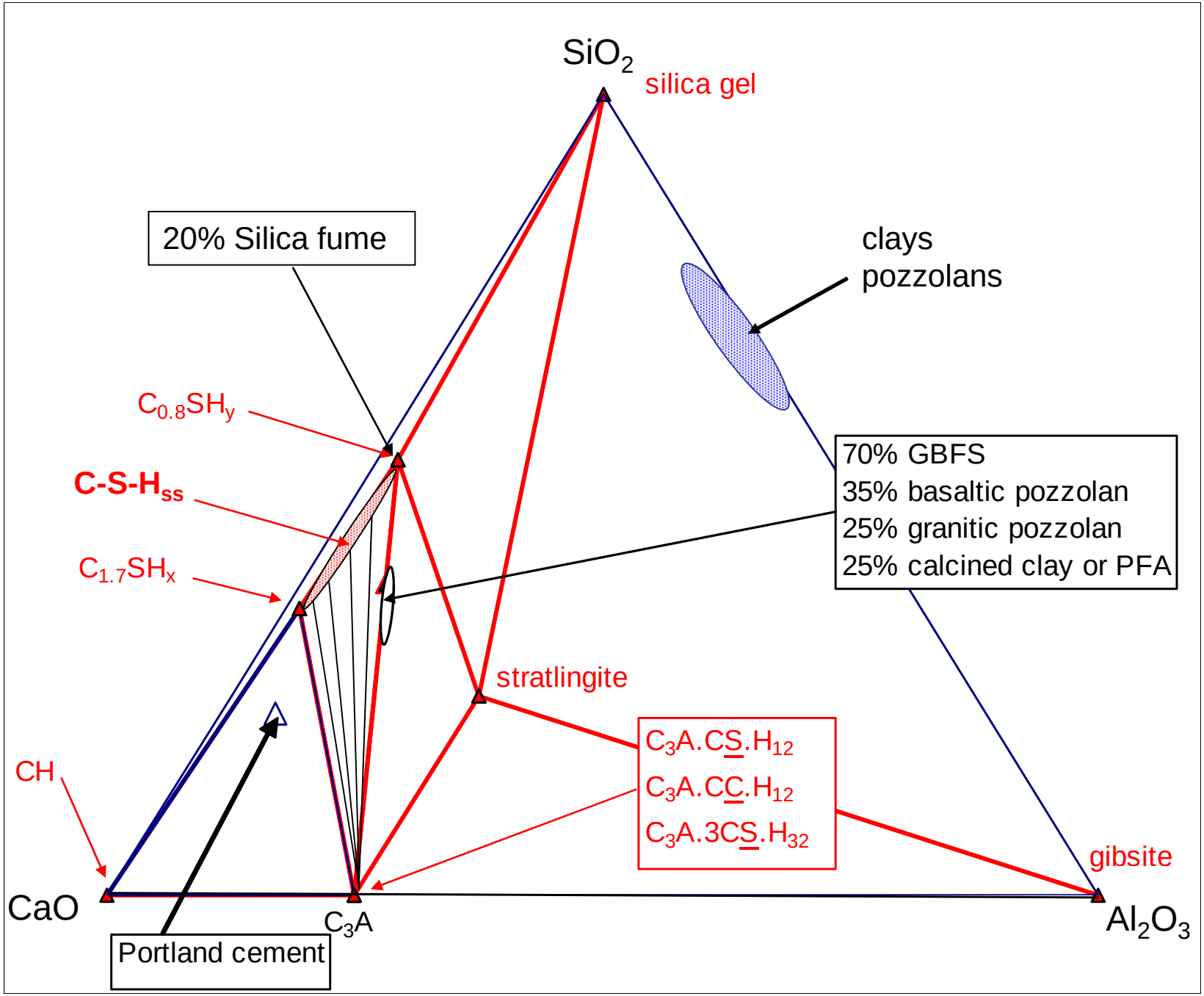
- maximum replacement with a non-calcareous pozzolana for same strength is c. 25%, and
- Except for N.America production of industrial SCMs falls well short of this in any event

Solutions to overcome this include developing

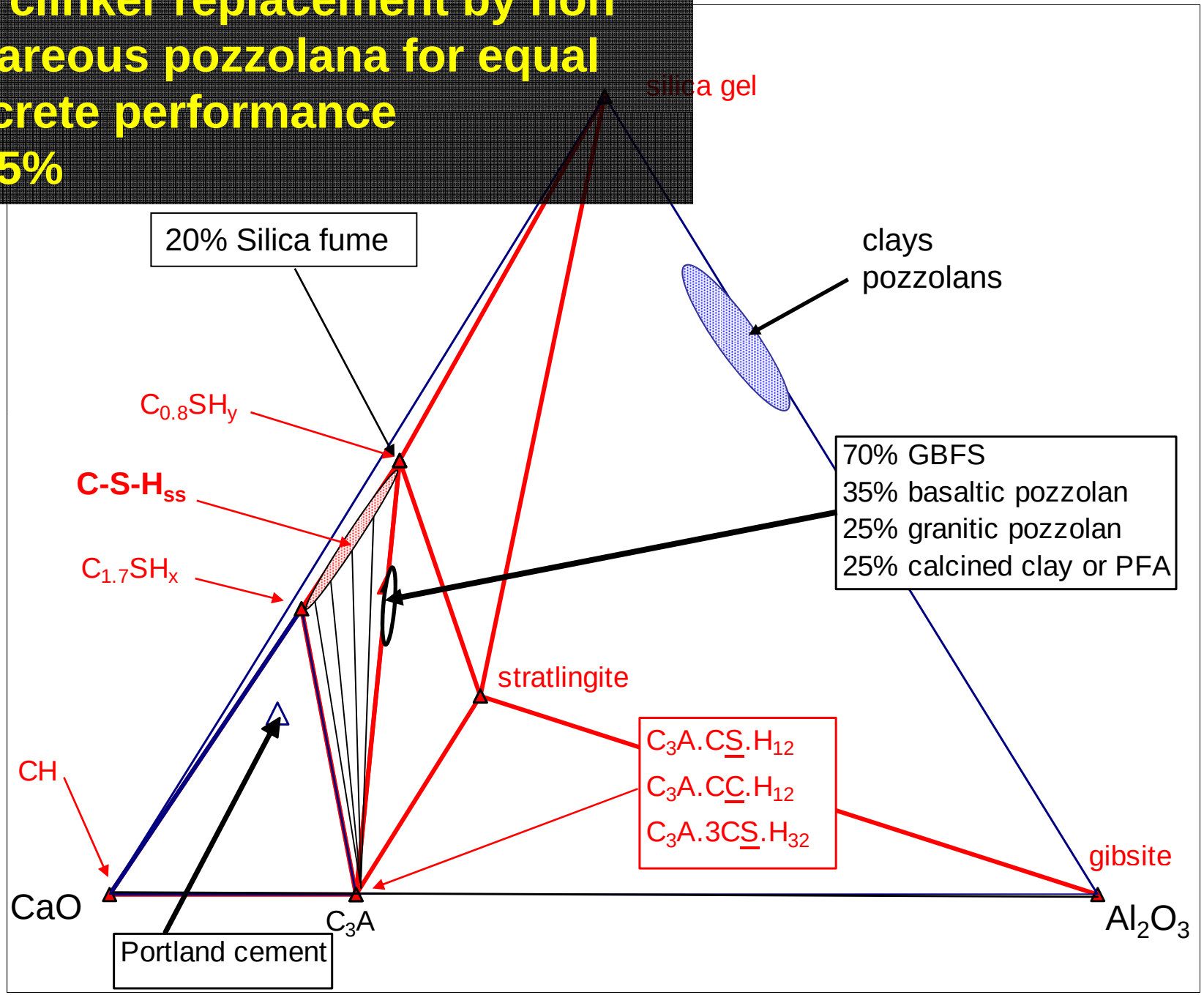
- natural pozzolana including calcined clays,
- the synergy between limestone and alumino silicate pozzolana for replacement up to 50%, and
- alkali activation for replacement higher than 50%


Global CO_2 emission from cement production
10^9 tonne pa
4
3
2
1
0
2008
2050
Improved kiln efficiency, use of bio fuels & natural gas (0.93 10^9 t CO_2)
40% SCM for same concrete performance (0.88 10^9 t CO_2)
1/5 of RM CO_2 recarbonated (0.34 10^9 t CO_2)
2/5 of CO_2 emissions captured and stored (0.83 10^9 t CO_2)
Currently 25% is about the limit for non calcareous SCMs


28d strengths, MPa
80
75
70
65
60
55
50
45
40
35
30
0
10
20
30
40
clinker replacement, %
siliceous fly ash
inert


SiO_2
silica gel
20% Silica fume
clays
pozzolans
$C_{0.8}SH_y$
C-S-H_{ss}
$C_{1.7}SH_x$
70% GBFS
35% basaltic pozzolan
25% granitic pozzolan
25% calcined clay or PFA
stratlingite
$C_3A.C\underline{S}.H_{12}$
$C_3A.C\underline{C}.H_{12}$
$C_3A.3C\underline{S}.H_{32}$
gibsite
CH
CaO
C_3A
Al_2O_3
Portland cement

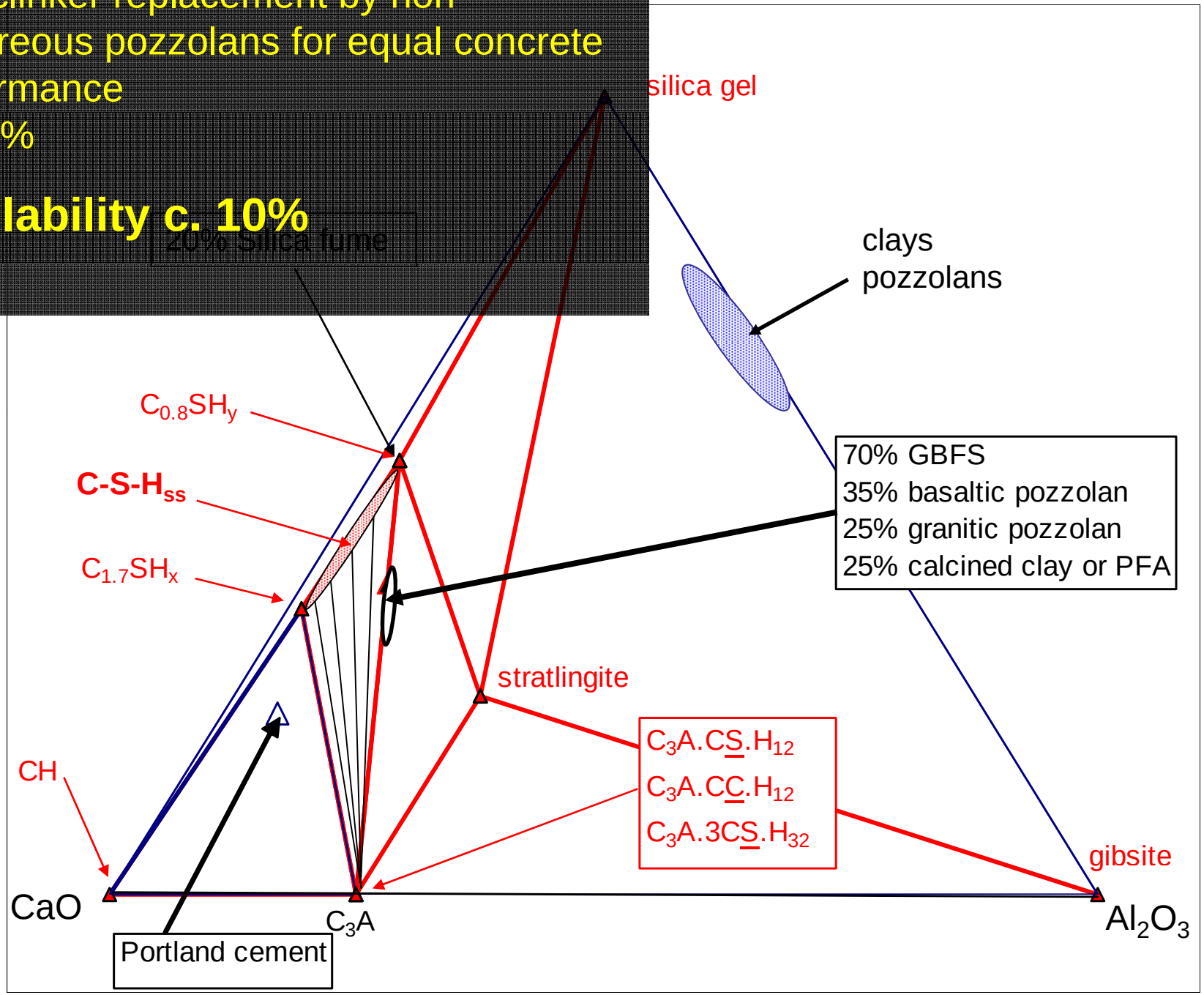
Max clinker replacement by non calcareous pozzolana for equal concrete performance
c. 25%



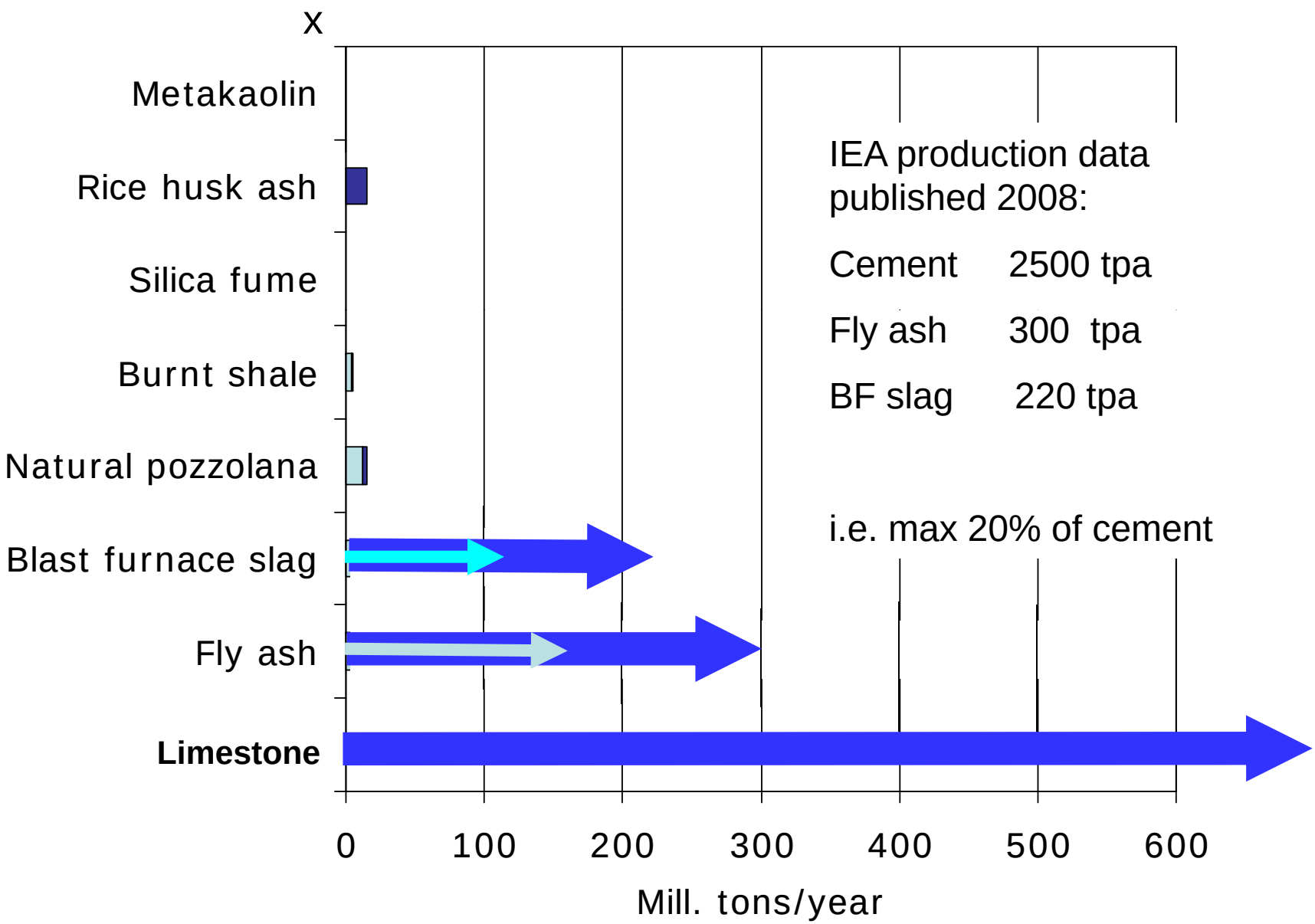
Max clinker replacement by non-calcareous pozzolans for equal concrete performance

c. 25%

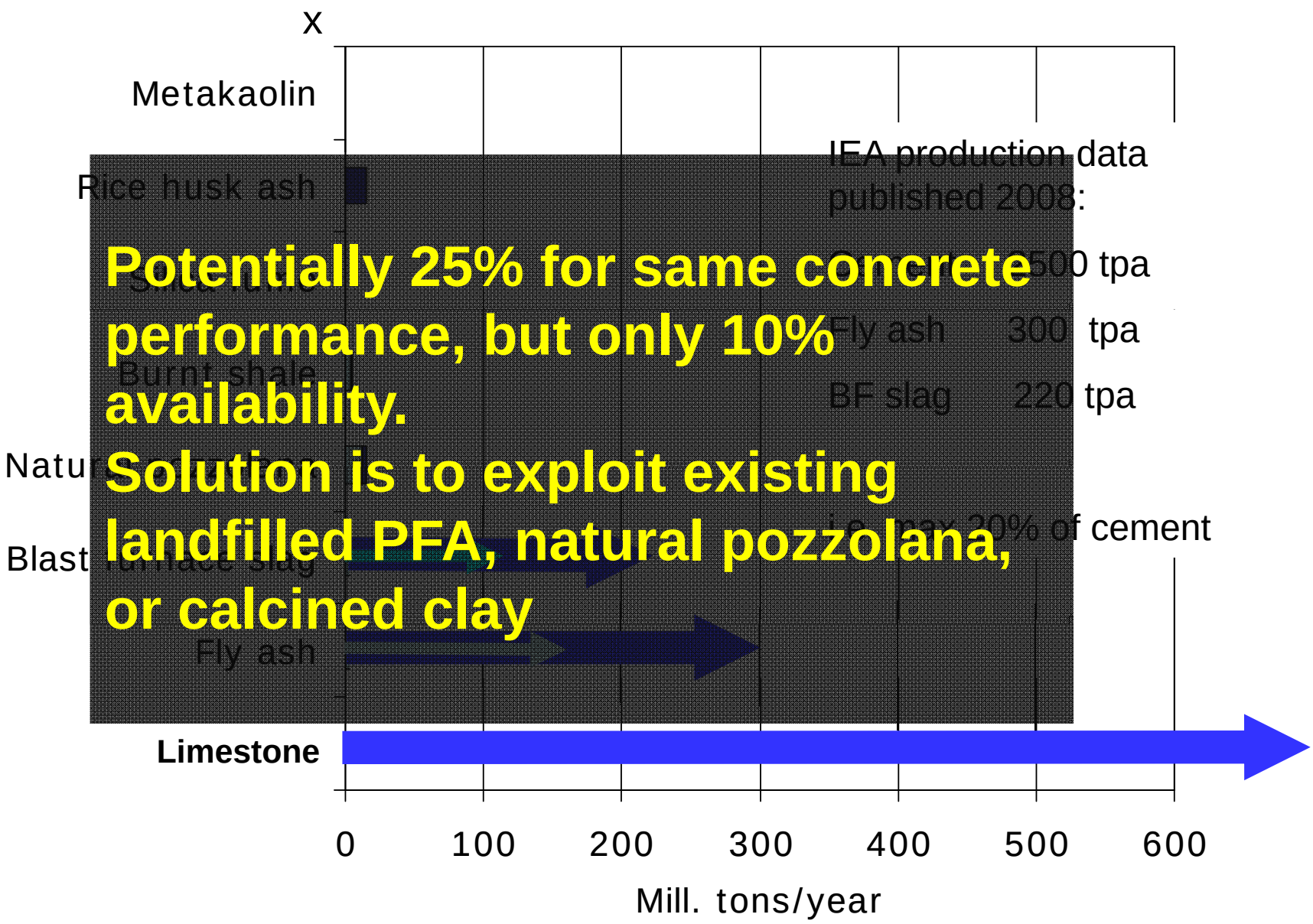
Availability c. 10%



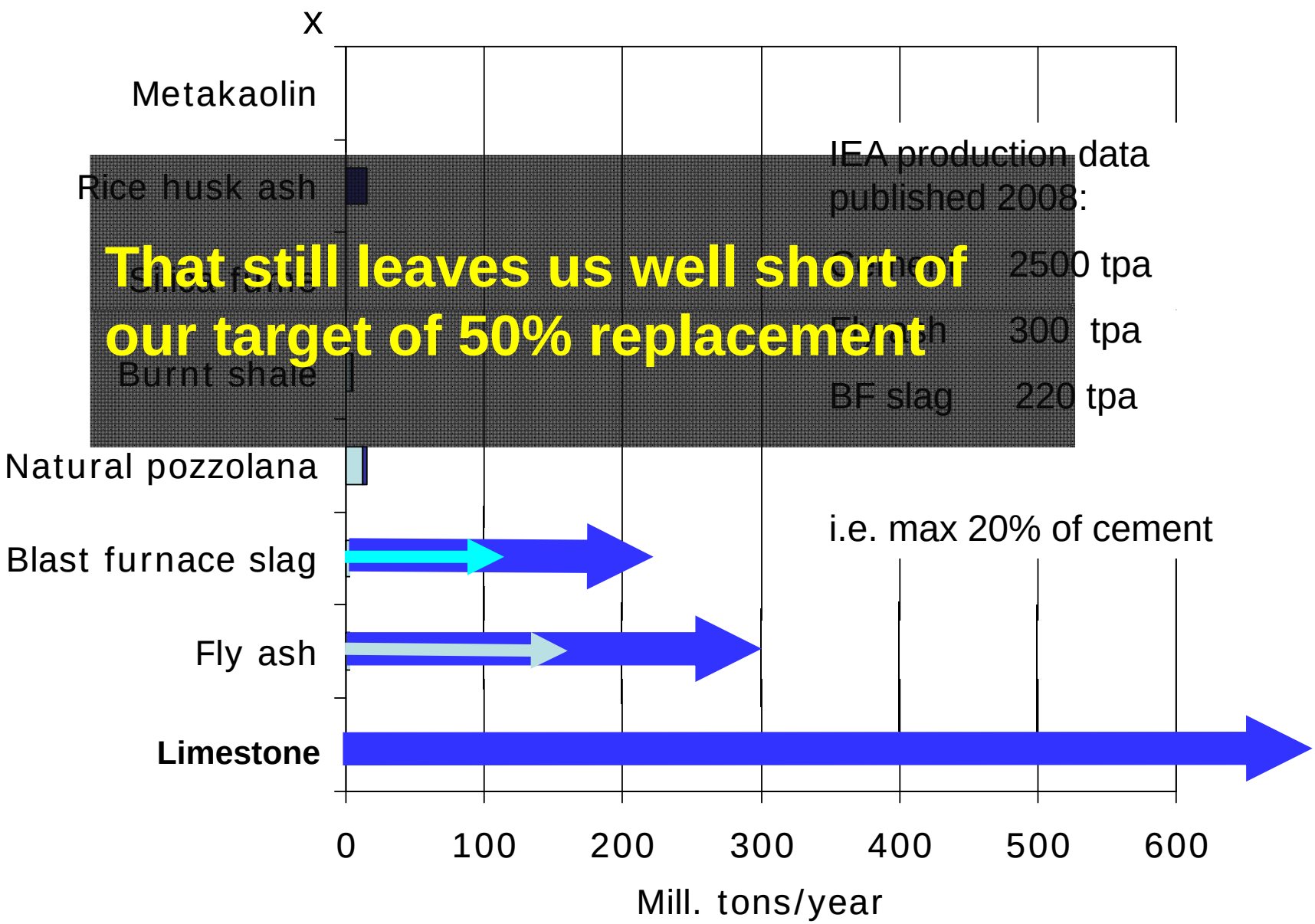
World wide availability of Supplementary Cementitious Materials

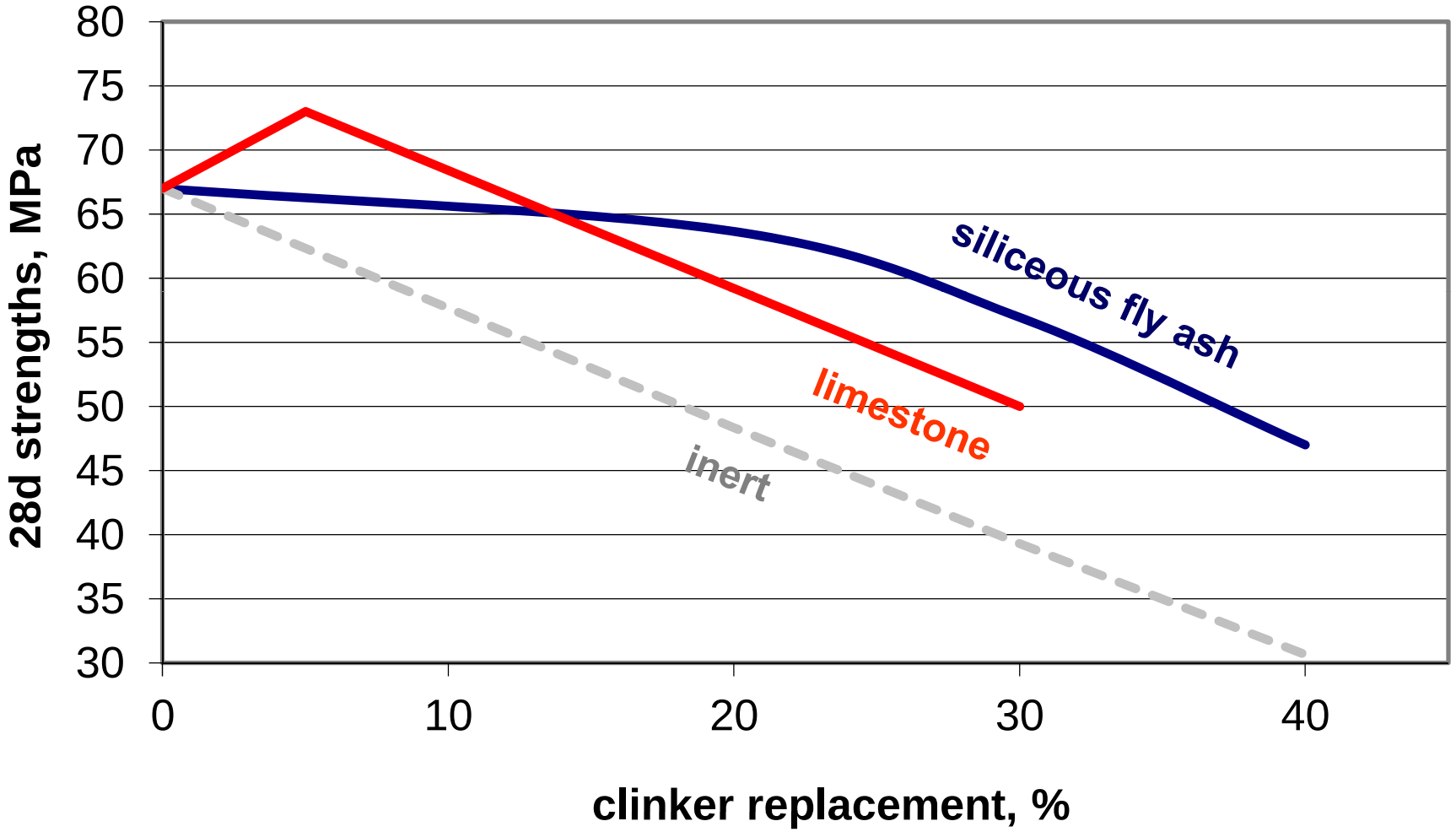


World wide availability of Supplementary Cementitious Materials

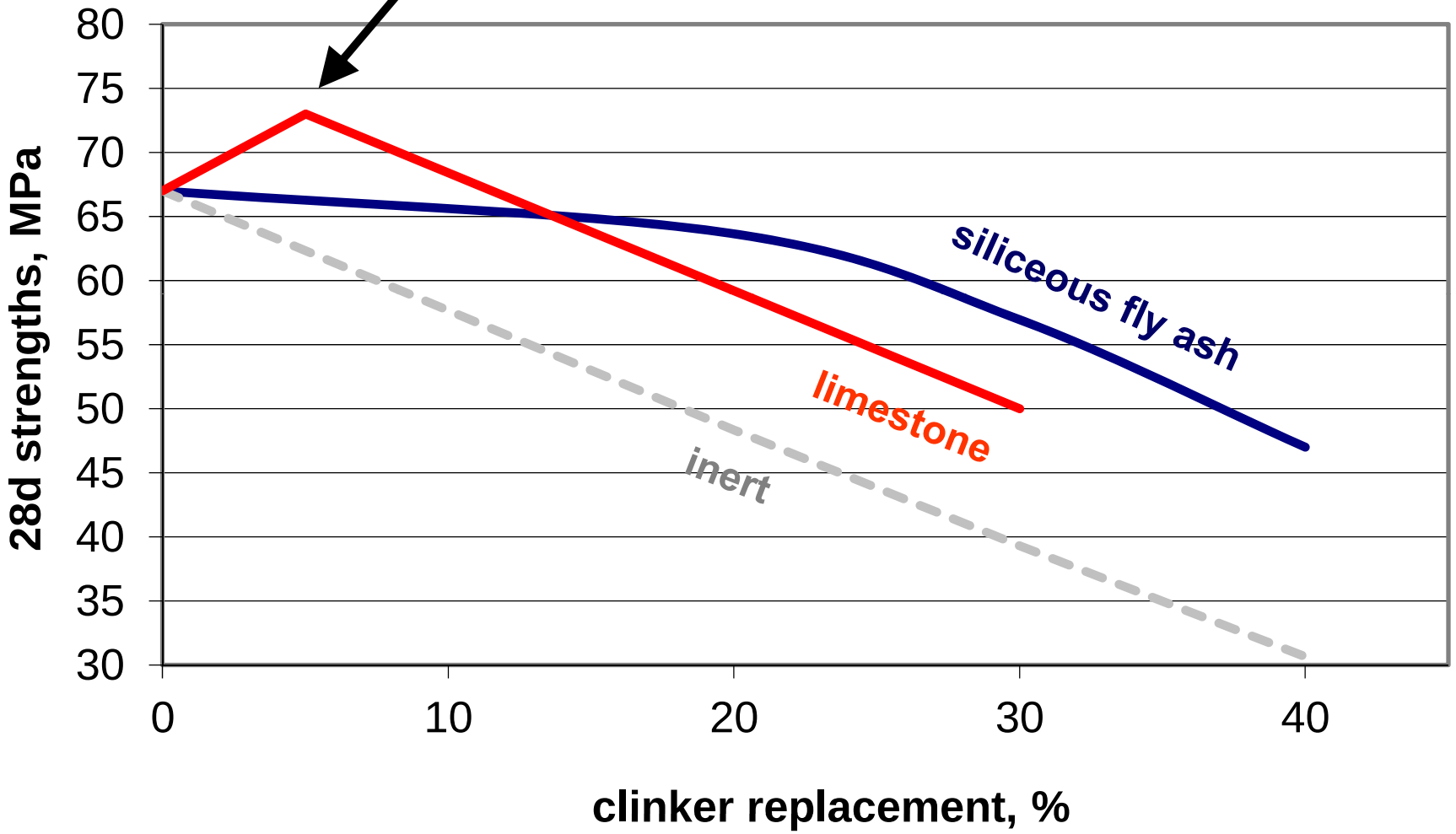


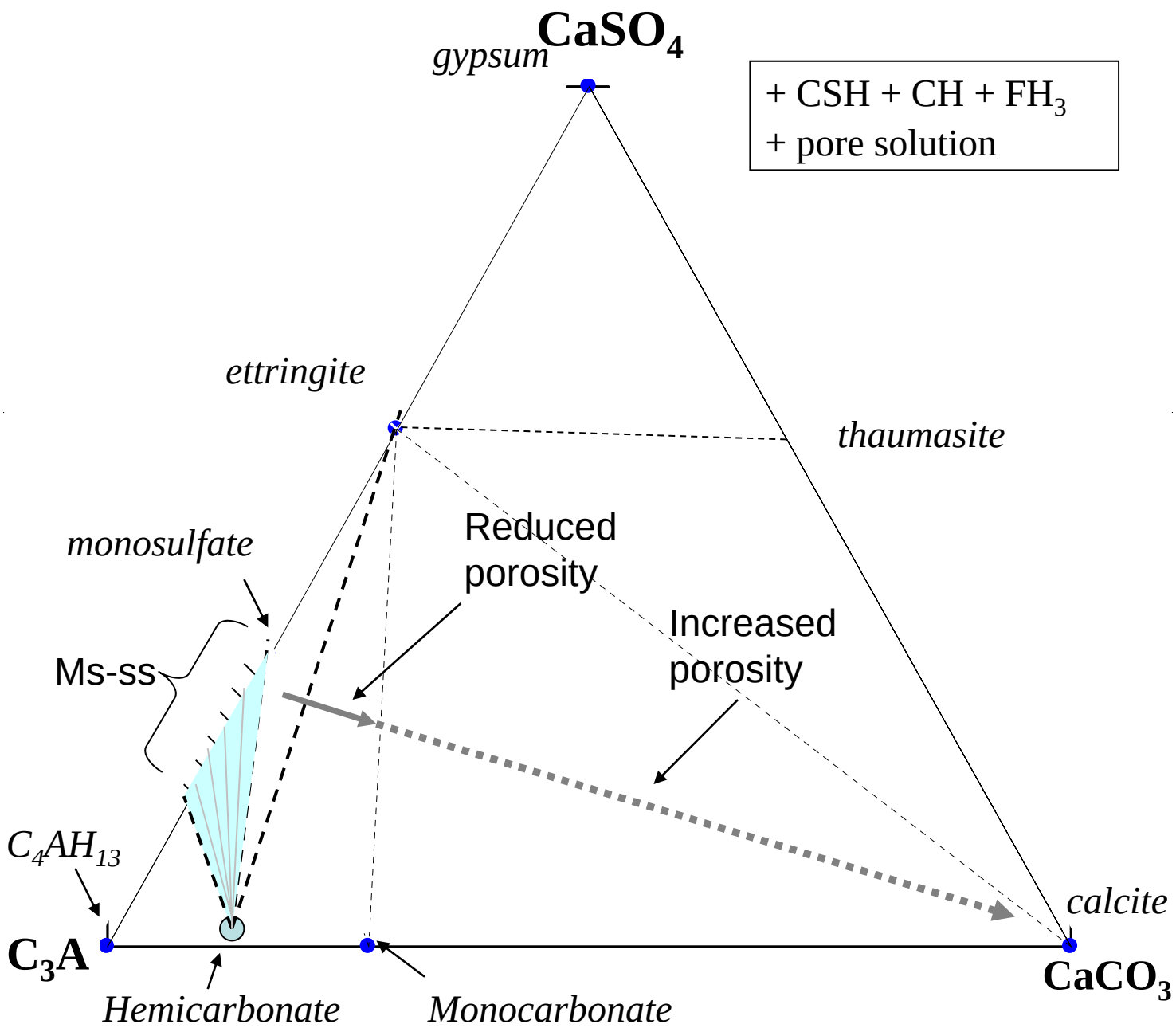
World wide availability of Supplementary Cementitious Materials

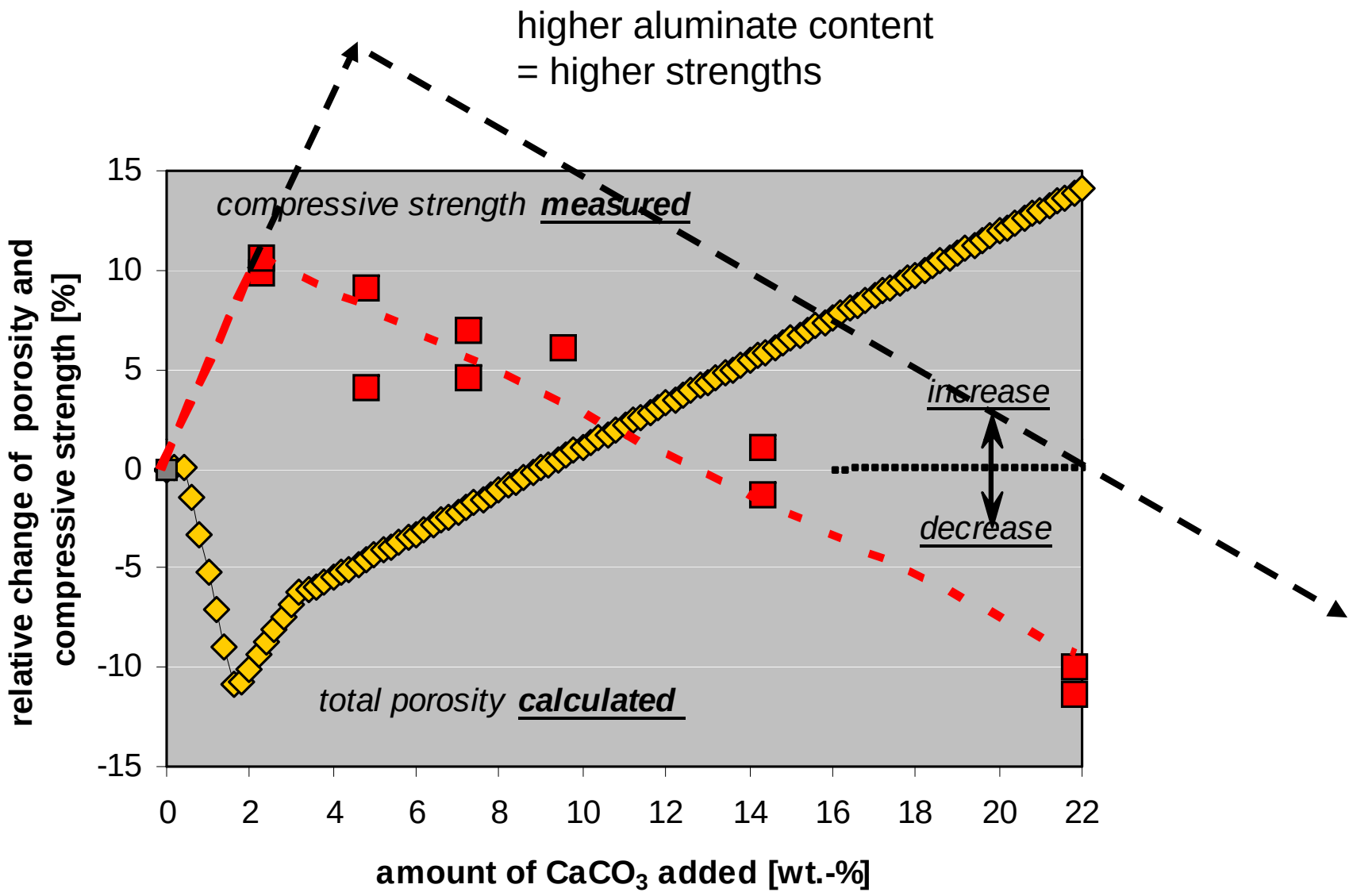



80
75
70
65
60
55
50
45
40
35
30
28d strengths, MPa
0
10
20
30
40
clinker replacement, %
siliceous fly ash
limestone
inert

The carboaluminate reaction suggests a way out.

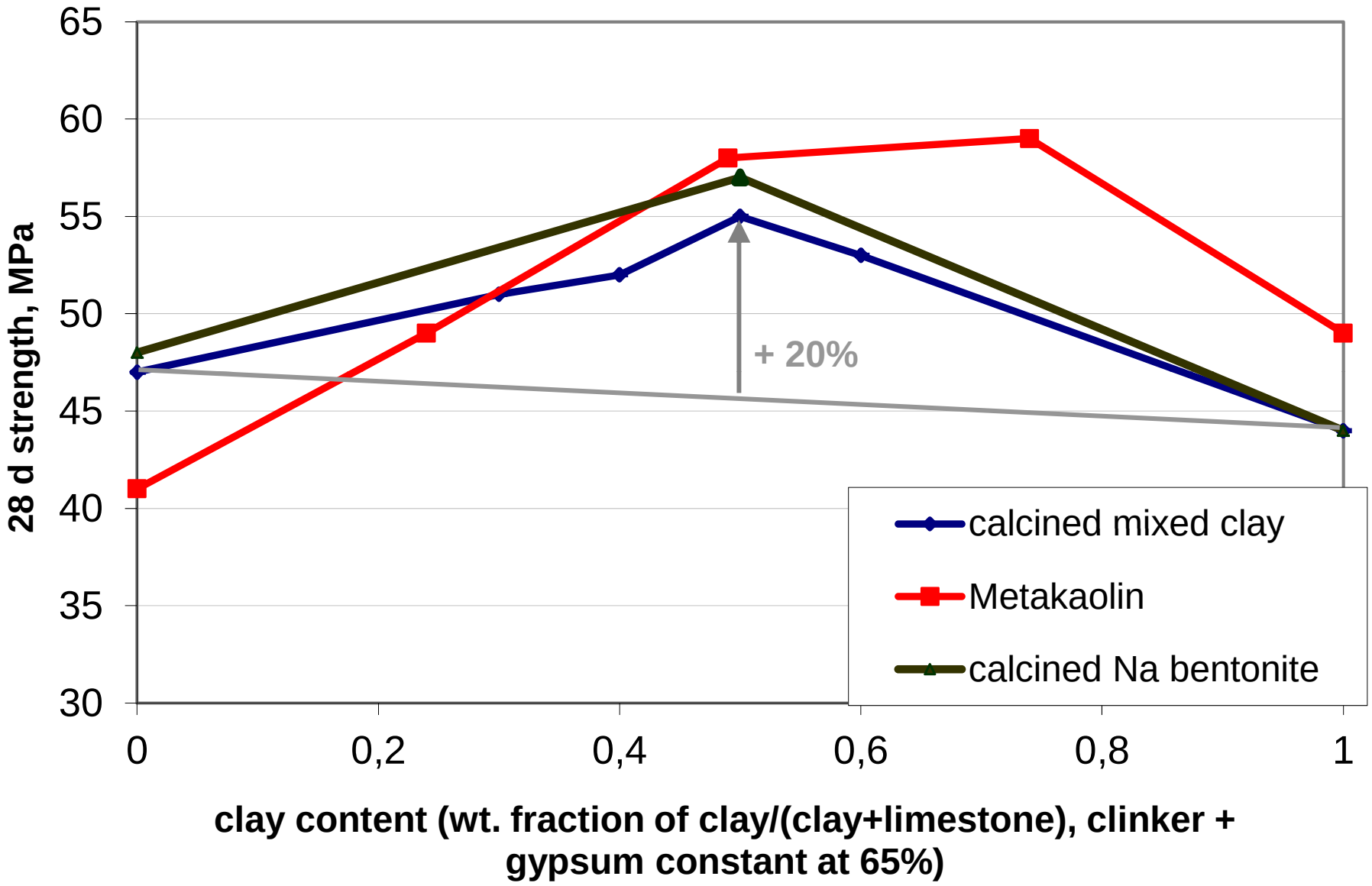


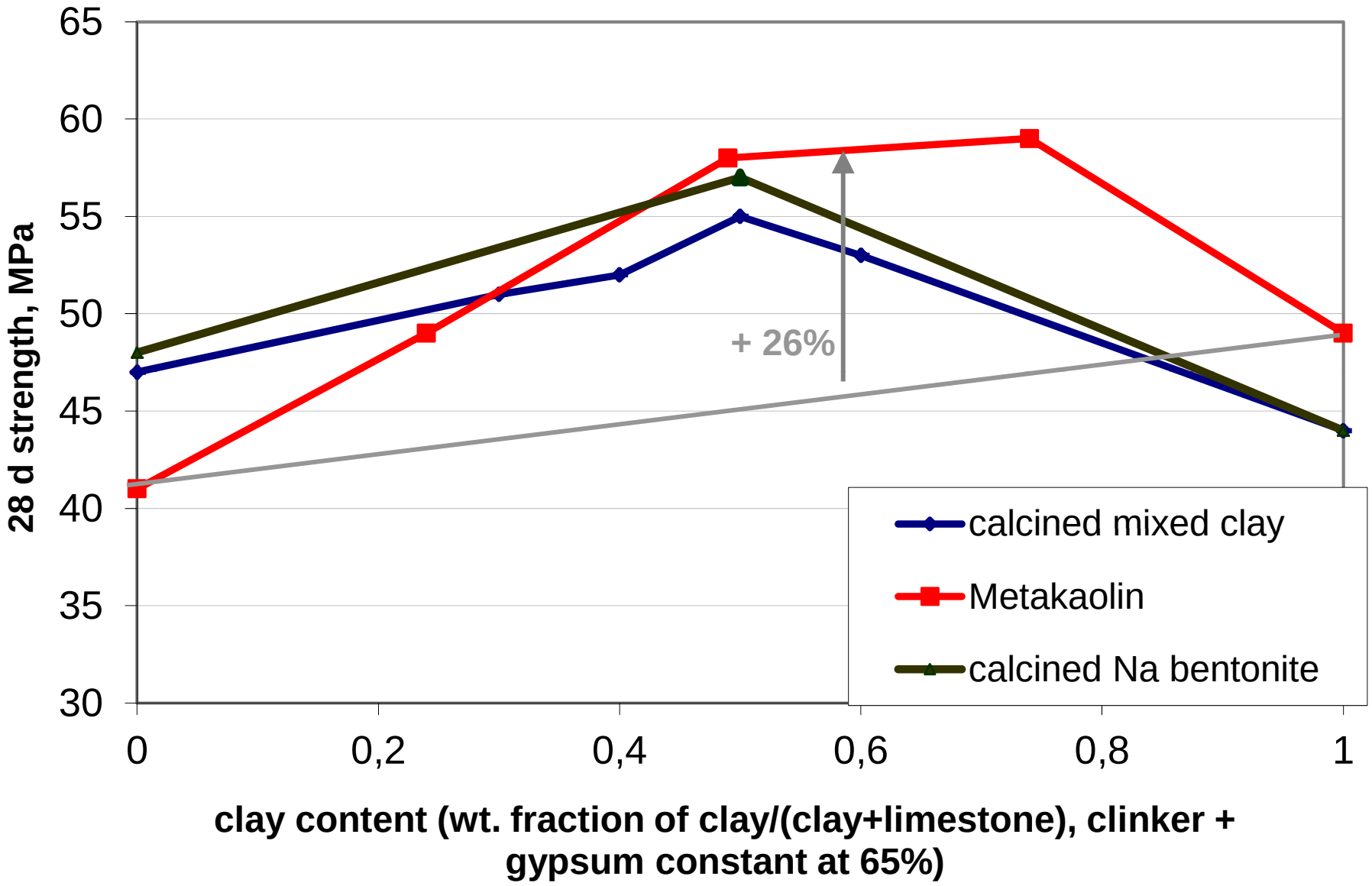

CaSO4
gypsum
+ CSH + CH + FH3
+ pore solution
ettringite
thaumasite
monosulfate
Reduced
porosity
Increased
porosity
Ms-ss
C4AH13
calcite
C3A
CaCO3
Hemicarbonate
Monocarbonate

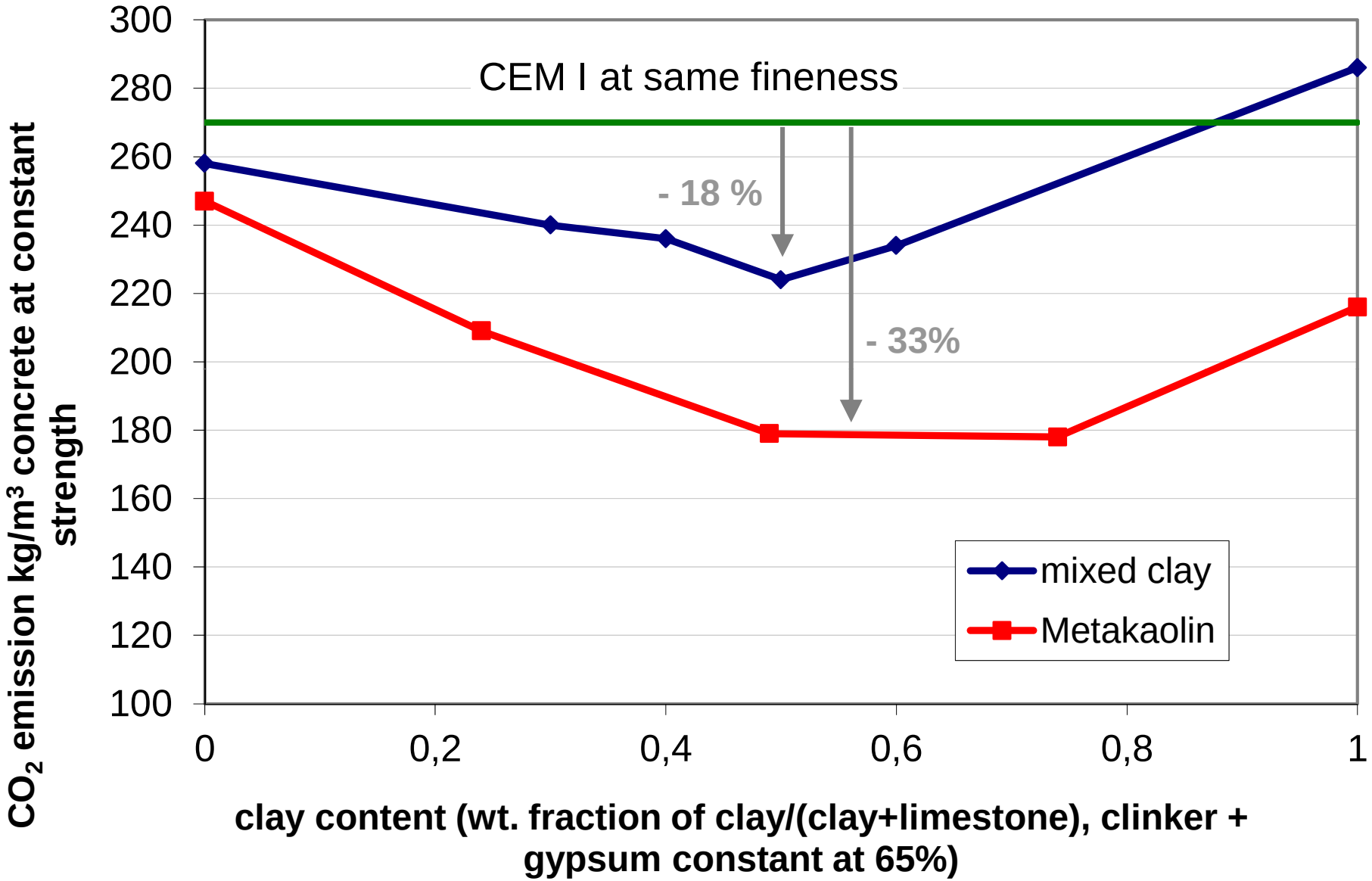


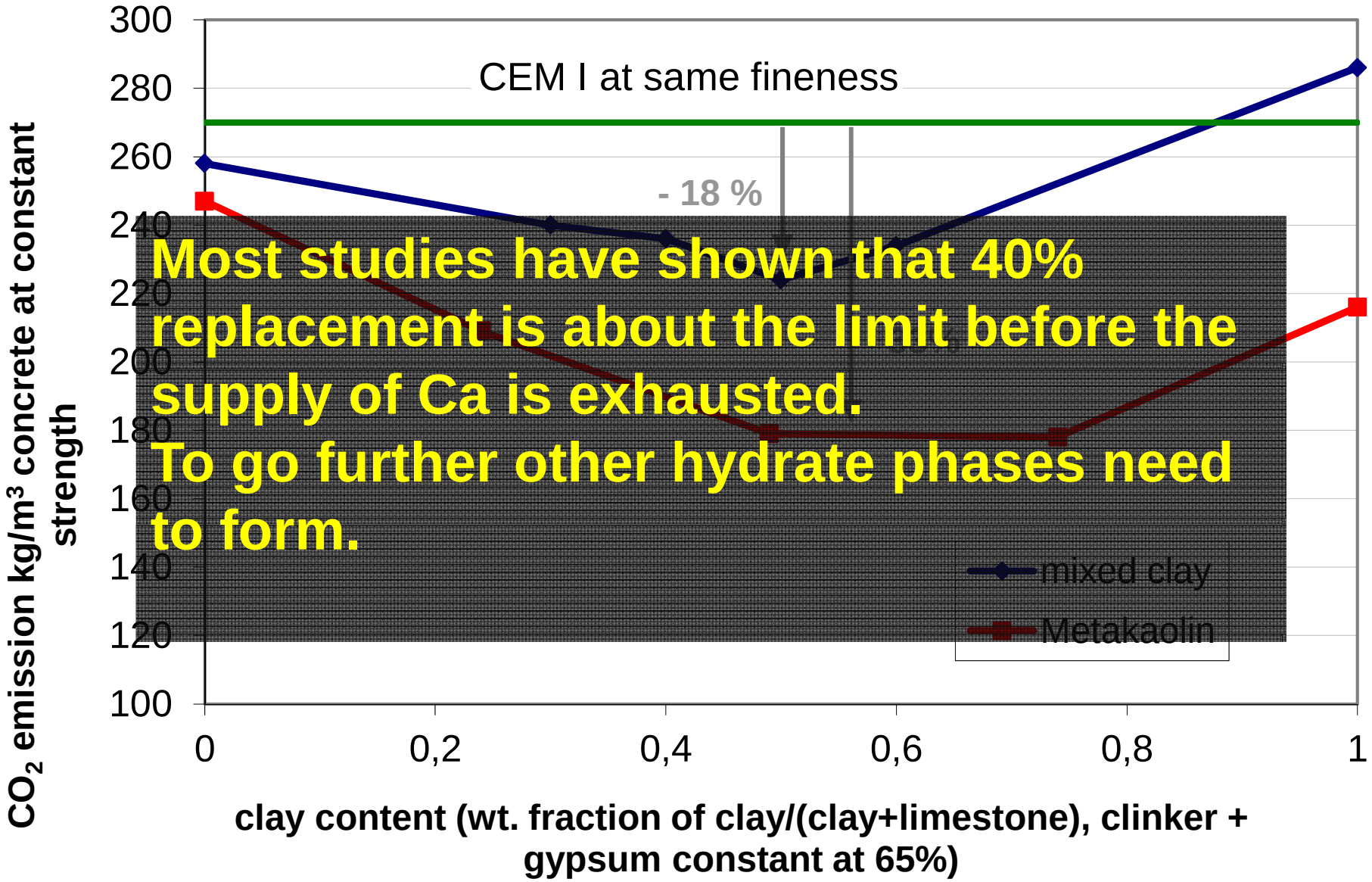
Very good correlation between predicted changes of relative porosity and measured compressive strength

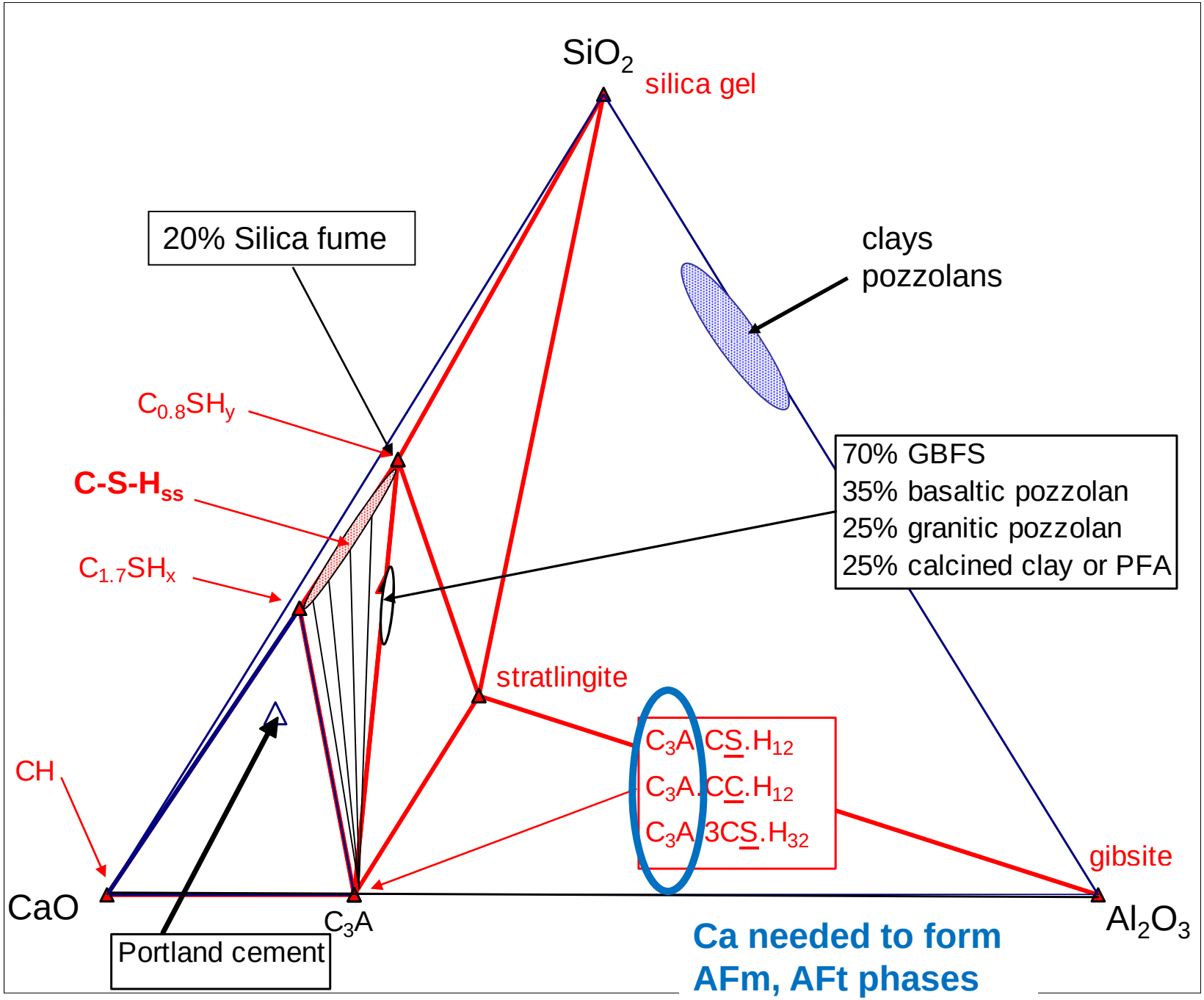

Limestone and calcined clay
Acc.V Spot Magn Det WD Exp
11.1 kV 3.2 5000x SE 10.6 1
5 µm

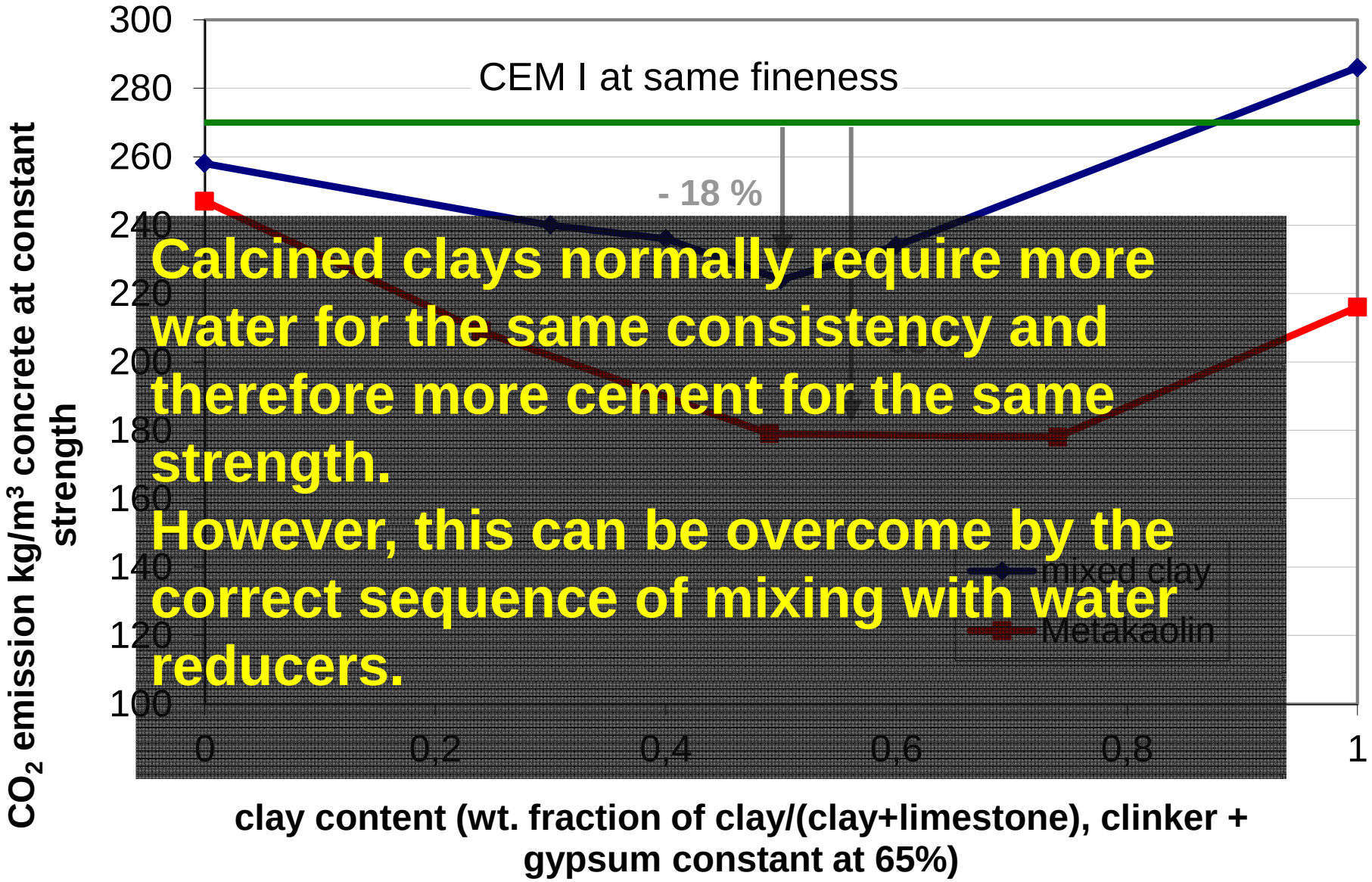

65
60
55
50
45
40
35
30
28 d strength, MPa
0
0,2
0,4
0,6
0,8
1
+ 20%
calcined mixed clay
Metakaolin
calcined Na bentonite
clay content (wt. fraction of clay/(clay+limestone), clinker + gypsum constant at 65%)


65
60
55
50
45
40
35
30
28 d strength, MPa
0
0,2
0,4
0,6
0,8
1
+ 26%
calcined mixed clay
Metakaolin
calcined Na bentonite
clay content (wt. fraction of clay/(clay+limestone), clinker + gypsum constant at 65%)


300
280
260
240
220
200
180
160
140
120
100
0
0,2
0,4
0,6
0,8
1
CEM I at same fineness
- 18 %
- 33%
mixed clay
Metakaolin
CO_2 emission kg/m³ concrete at constant strength
clay content (wt. fraction of clay/(clay+limestone), clinker + gypsum constant at 65%)

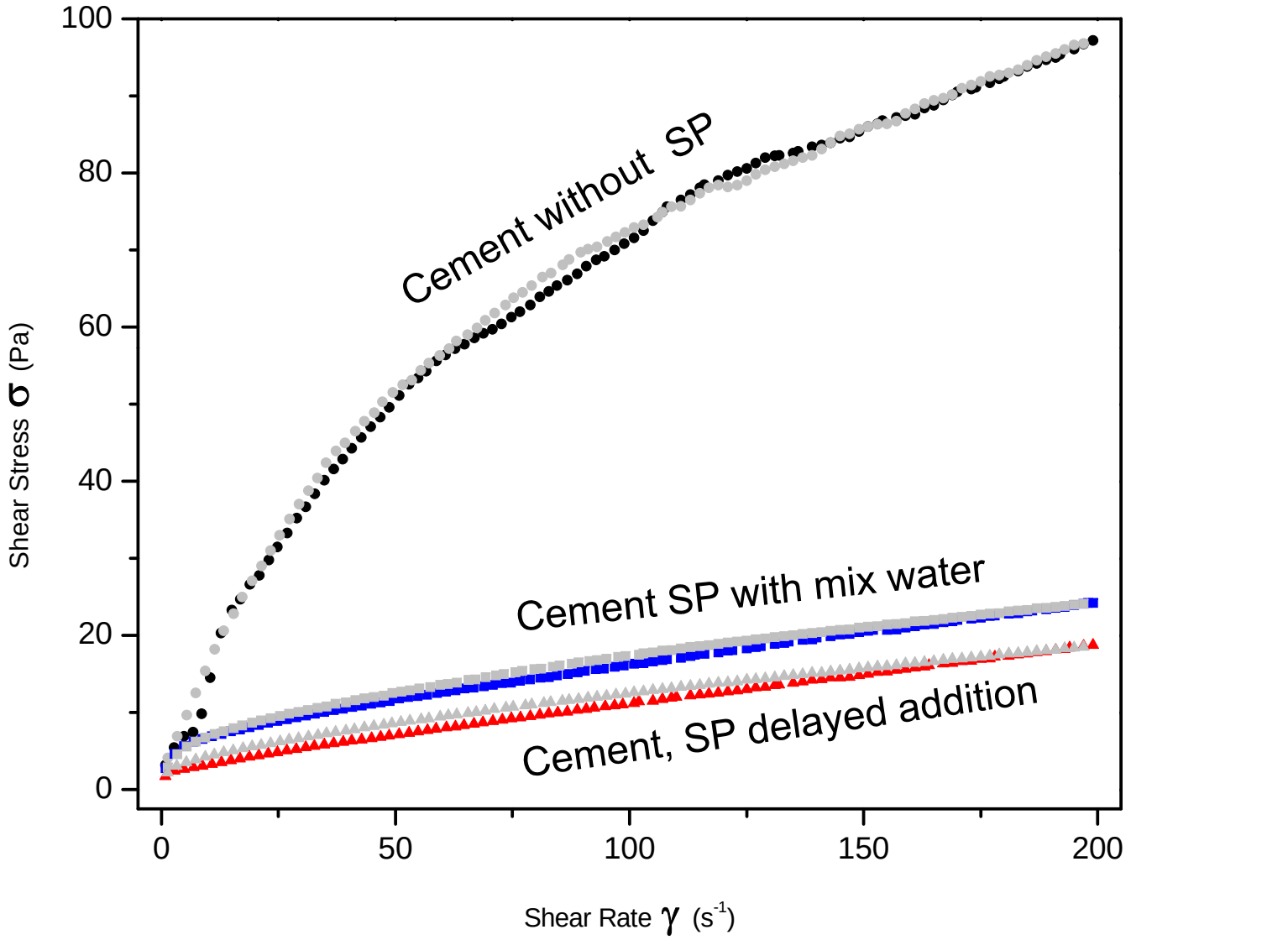

300
280
260
240
220
200
180
160
140
120
100
0
0,2
0,4
0,6
0,8
1
CEM I at same fineness
- 18 %
Most studies have shown that 40% replacement is about the limit before the supply of Ca is exhausted.
To go further other hydrate phases need to form.
mixed clay
Metakaolin
CO2 emission kg/m3 concrete at constant strength
clay content (wt. fraction of clay/(clay+limestone), clinker + gypsum constant at 65%)

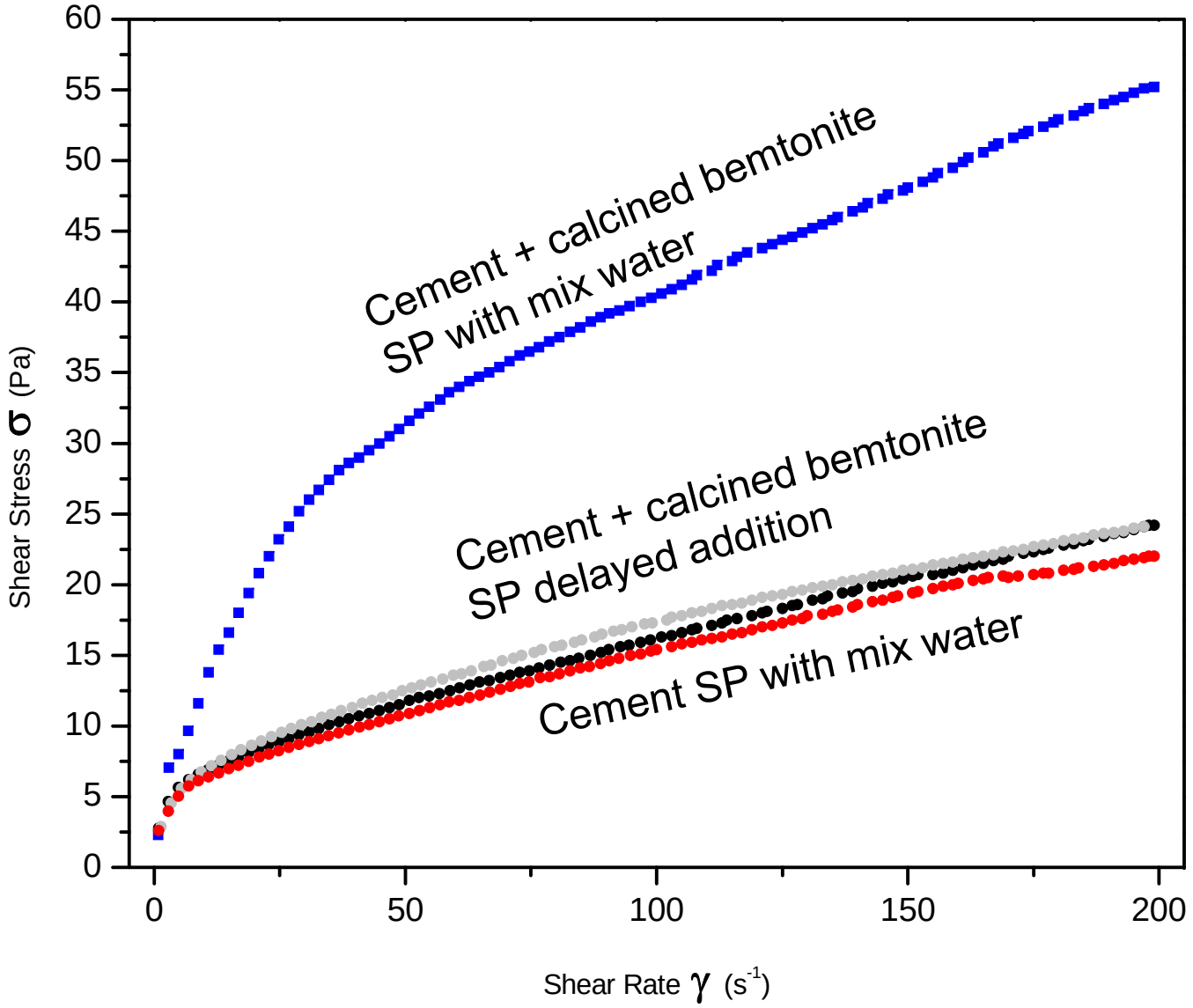

SiO_2
silica gel
20% Silica fume
clays
pozzolans
$C_{0.8}SH_y$
C-S-H$_{ss}$
$C_{1.7}SH_x$
70% GBFS
35% basaltic pozzolan
25% granitic pozzolan
25% calcined clay or PFA
stratlingite
$C_3A.\underline{C}S.H_{12}$
$C_3A.C\underline{C}.H_{12}$
$C_3A.3C\underline{S}.H_{32}$
gibsite
CH
CaO
C_3A
Al_2O_3
Portland cement
Ca needed to form AFm, AFt phases



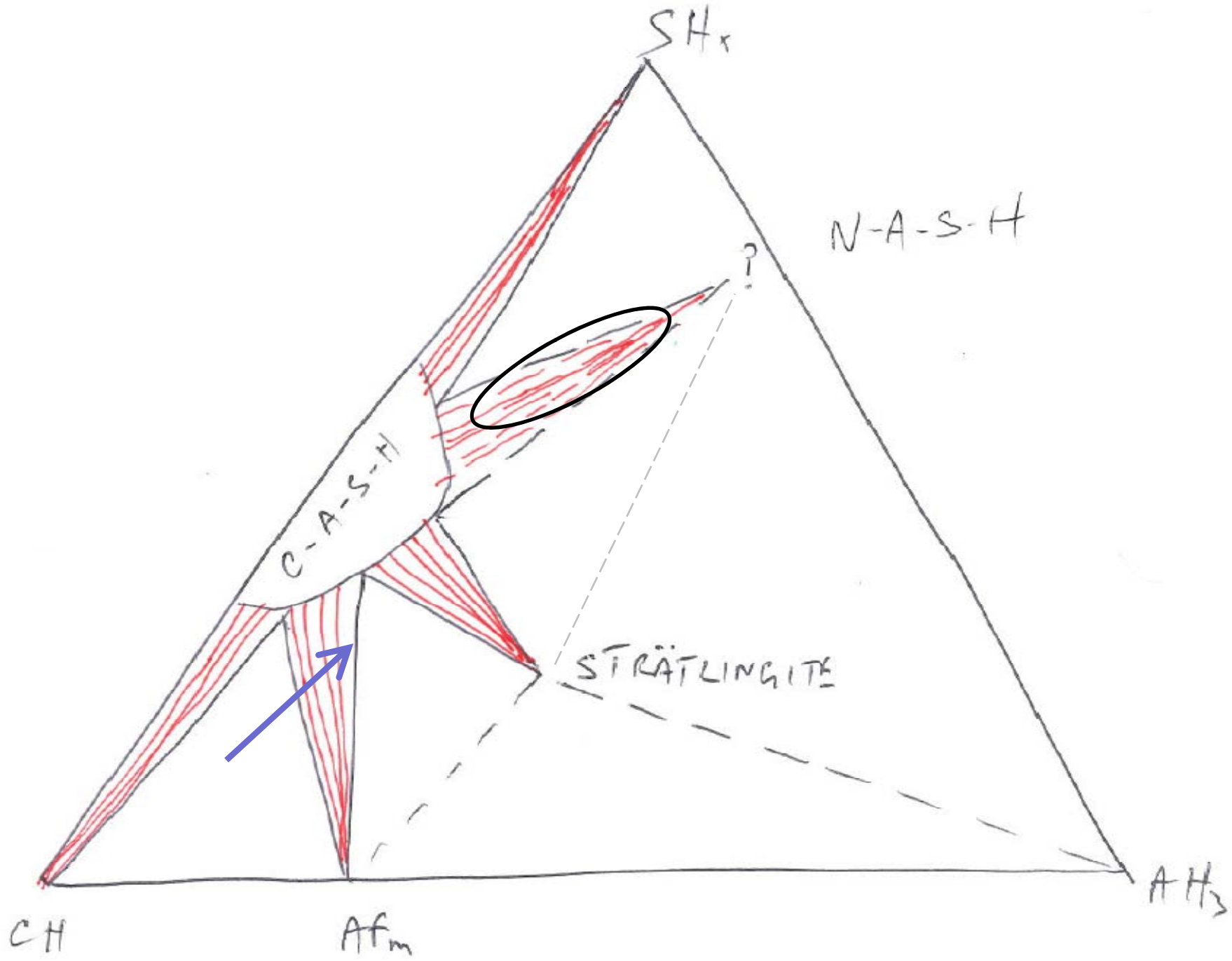
Calcined clays normally require more water for the same consistency and therefore more cement for the same strength.

However, this can be overcome by the correct sequence of mixing with water reducers.

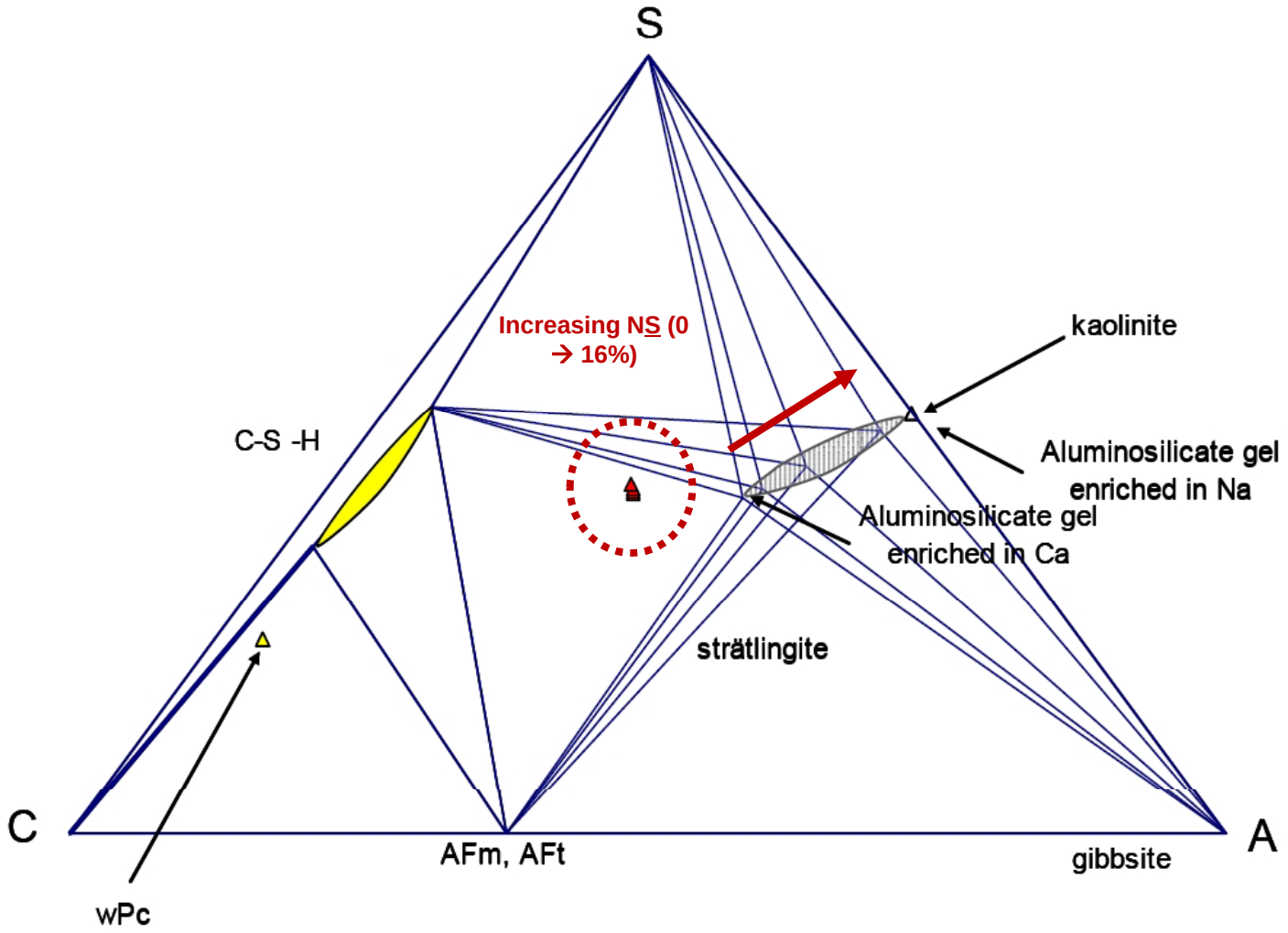

0.6% SP
w/b = 0.5
35% replacement
Cement without SP
Cement SP with mix water
Cement, SP delayed addition
Shear Stress σ (Pa)
Shear Rate γ (s-1)
0
20
40
60
80
100
0
50
100
150
200


Cement + calcined bemtonite
SP with mix water
Cement + calcined bemtonite
SP delayed addition
Cement SP with mix water
Shear Stress σ (Pa)
Shear Rate γ (s-1)
0
5
10
15
20
25
30
35
40
45
50
55
60
0
50
100
150
200

Alkali activated calcined clay and portland cement


SH_x
N-A-S-H
?
C-A-S-H
STRÄTLINGITE
AH_3
CH
Af_m

STRUCTURAL EVOLUTION ASSESSMENT

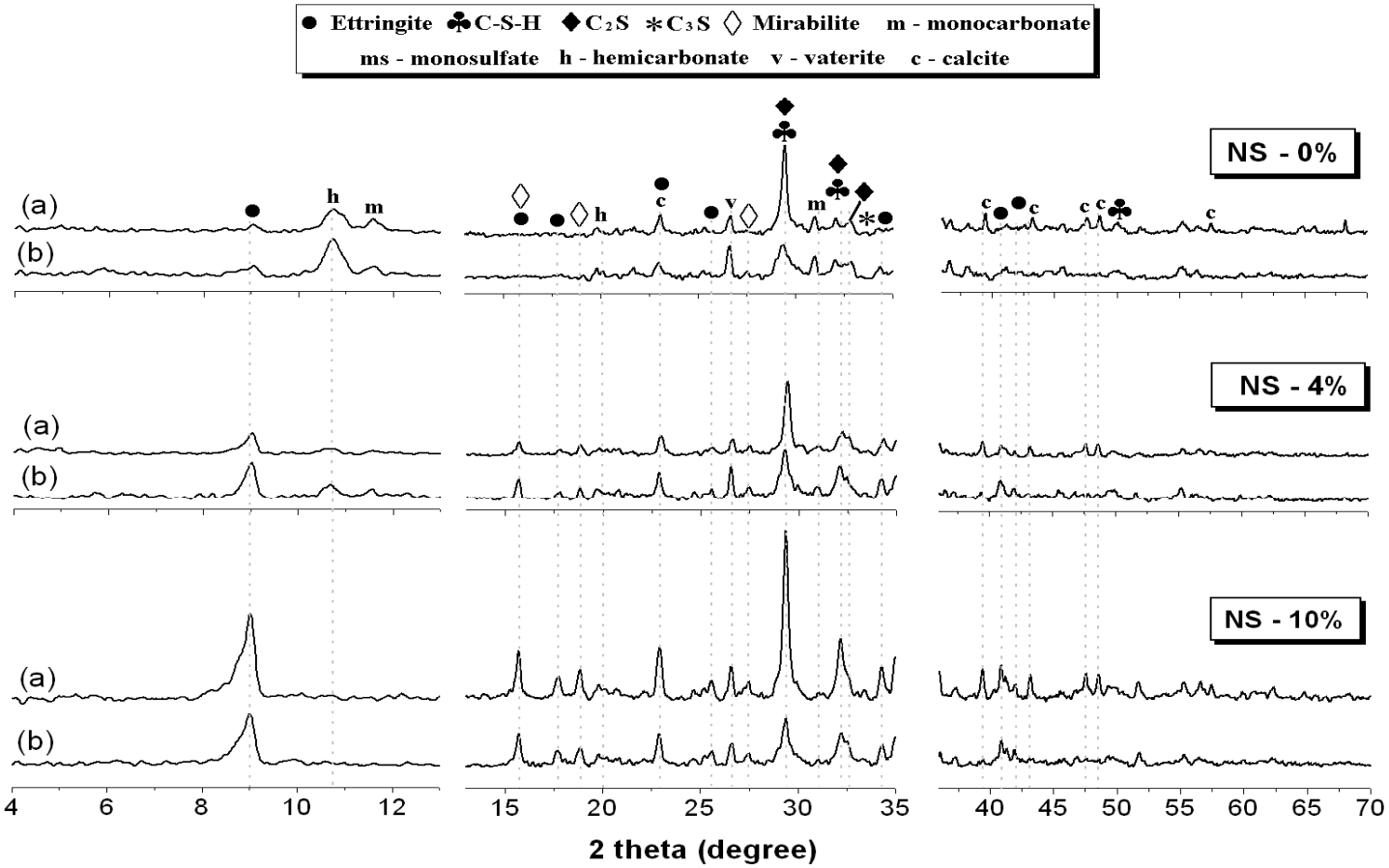


40 % clinker, MK/(MK+ls) ratio = **0.96**, sodium sulfate content **= 0, 4, 10, 16 %**

Constant water/binder ratio of **0.57**

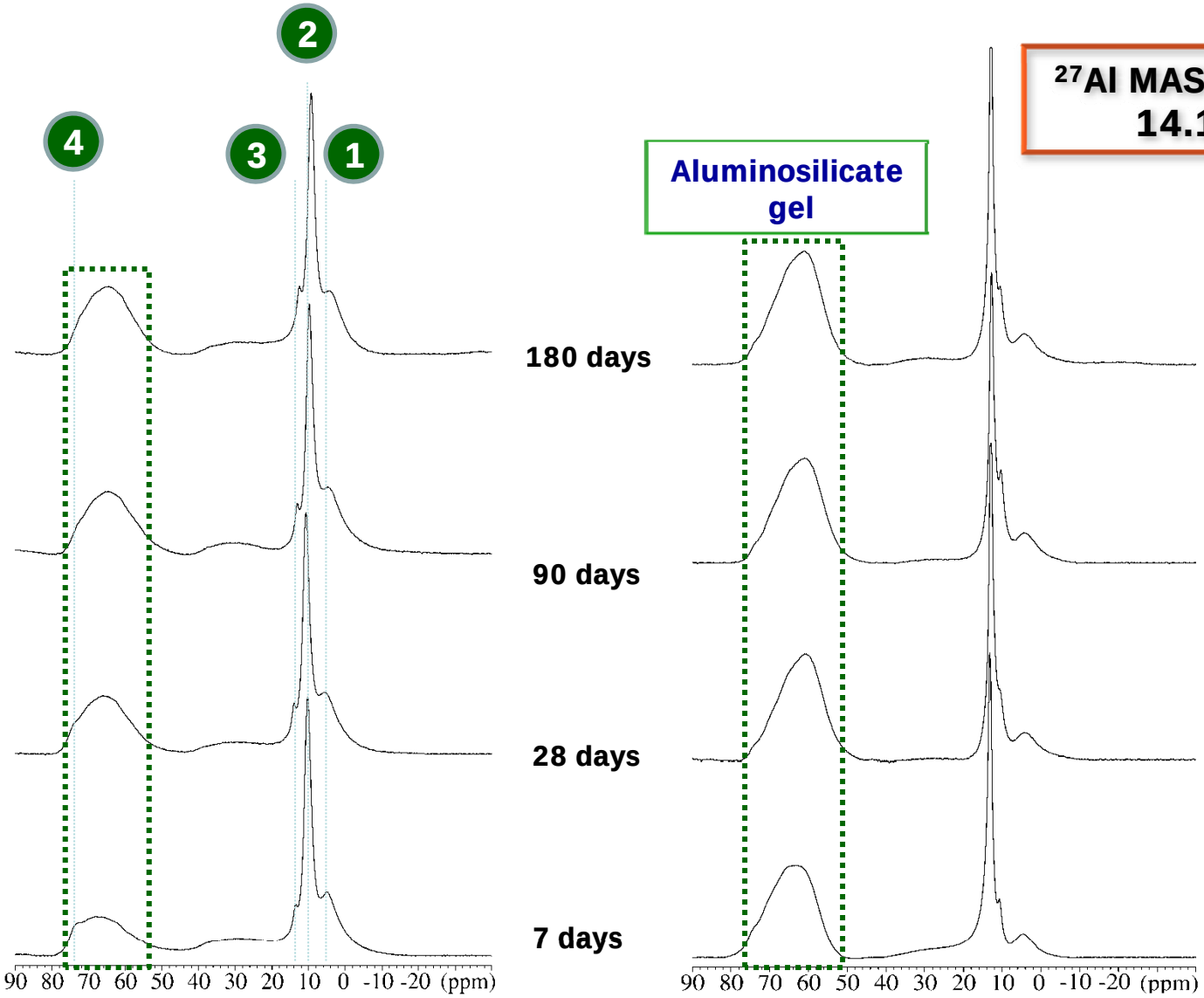
EFFECT OF MK/LIMESTONE RATIO ON STRUCTURE

X-RAY DIFFRACTION – 90 DAYS OF CURING – 40% CLINKER



MK/(MK+ls) ratio: a) 0.80 and b) 0.96

STRUCTURAL EVOLUTION ASSESSMENT



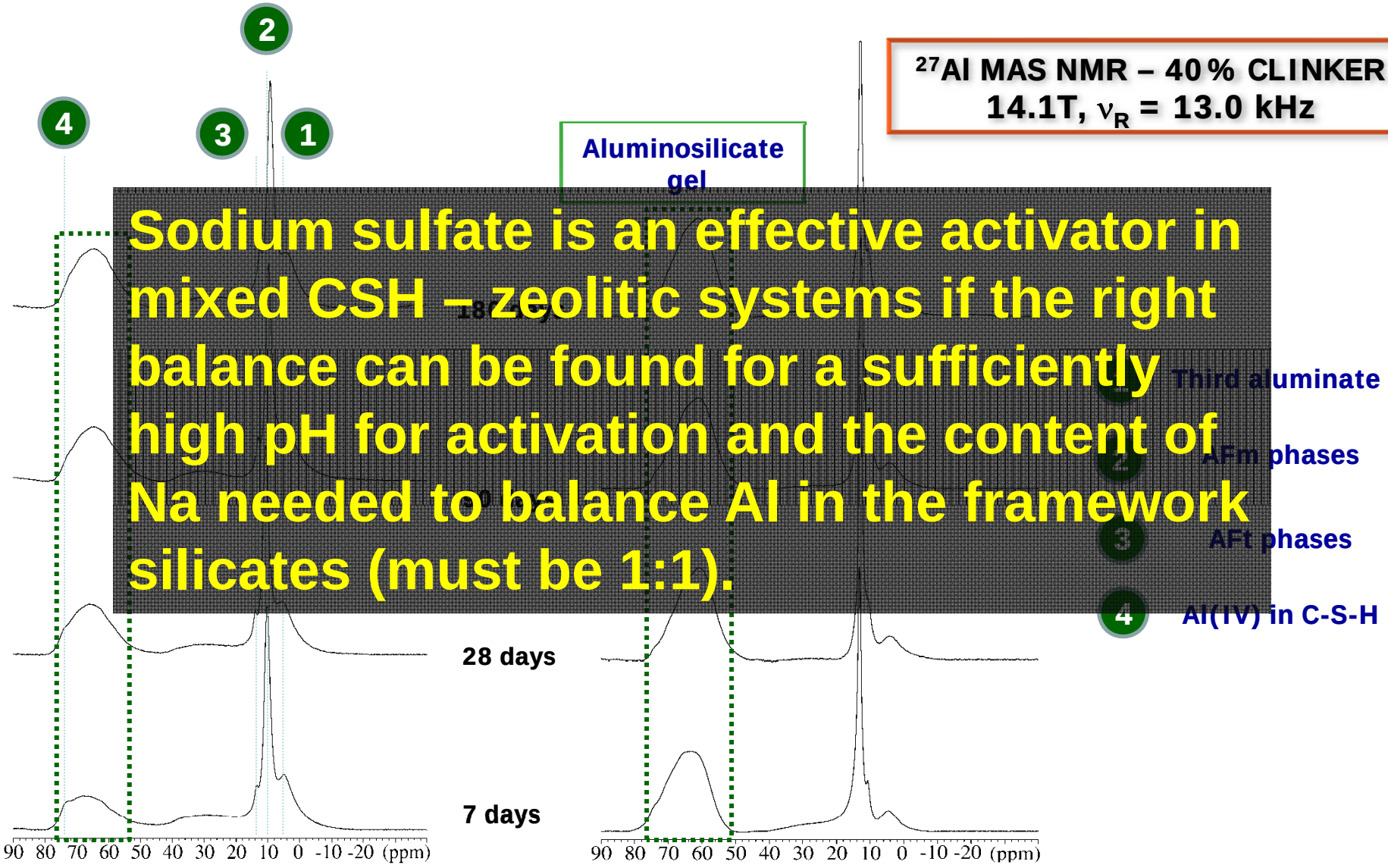
^{27}Al MAS NMR – 40 % CLINKER
14.1T, ν_R = 13.0 kHz

1. Third aluminate
2. AFm phases
3. AFt phases
4. Al(IV) in C-S-H

NS = 0 %

NS = 16 %

STRUCTURAL EVOLUTION ASSESSMENT



^{27}Al MAS NMR – 40 % CLINKER
14.1T, ν_R = 13.0 kHz

Sodium sulfate is an effective activator in mixed CSH – zeolitic systems if the right balance can be found for a sufficiently high pH for activation and the content of Na needed to balance Al in the framework silicates (must be 1:1).

3 Third aluminate

2 AFm phases

3 AFt phases

4 Al(IV) in C-S-H

NS = 0 %

NS = 16 %

Conclusion

By combining limestone and alumino silicate pozzolana (FA, calcined clay etc.), the levels of clinker replacement for the same concrete performance can be extended from about 25% to 40%.

For further levels of replacement, alkalis for activation and stabilisation of framework silicates are needed.