Wiesław Kurdowski and Paweł Pichniarczyk

The Troubles with Ettringite Expansion

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The Troubles with Ettringite Expansion

Ettringite is a quickly formed phase in the cement hydration process and easily detectable by XRD after 10 min

But what form is prevailing ?

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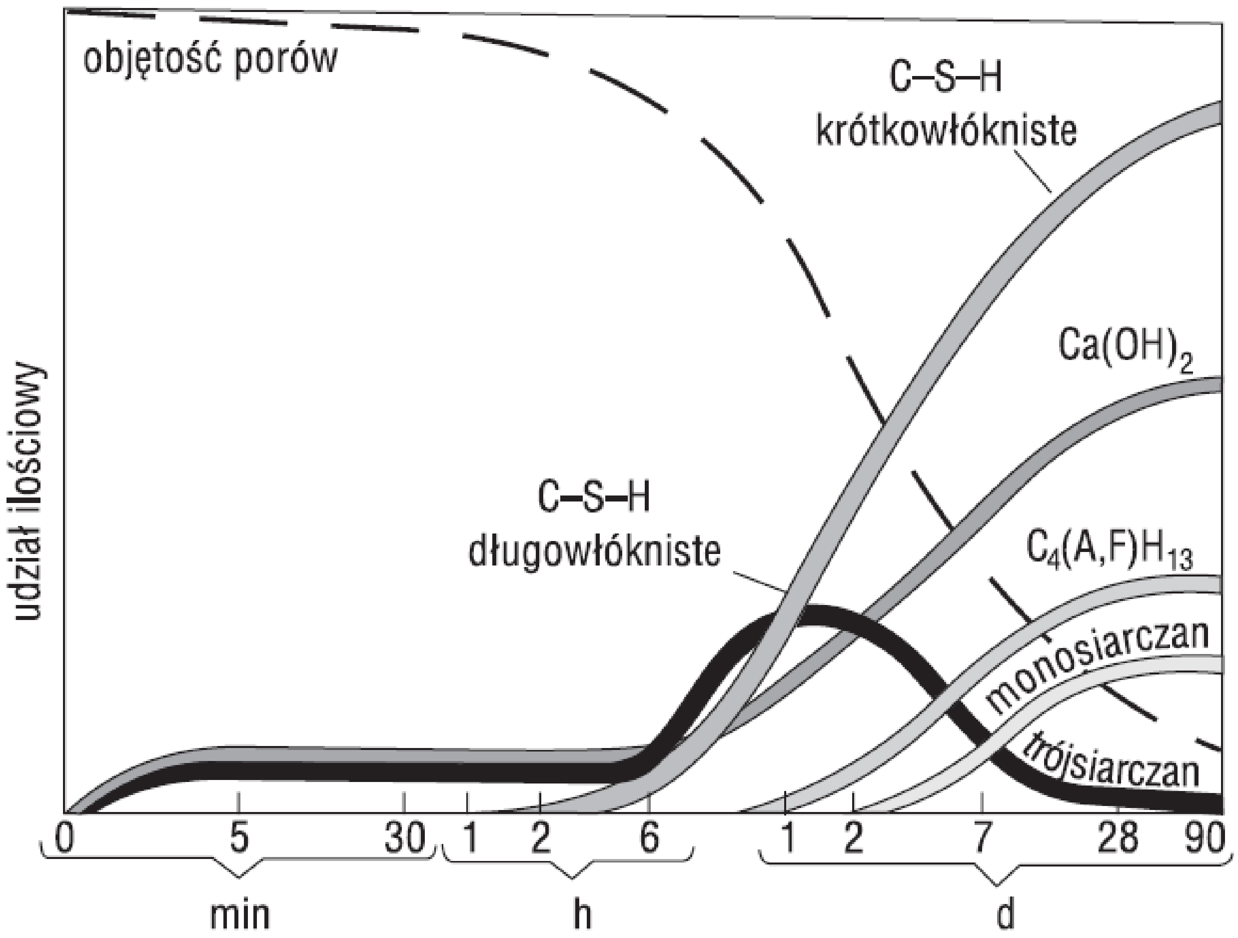
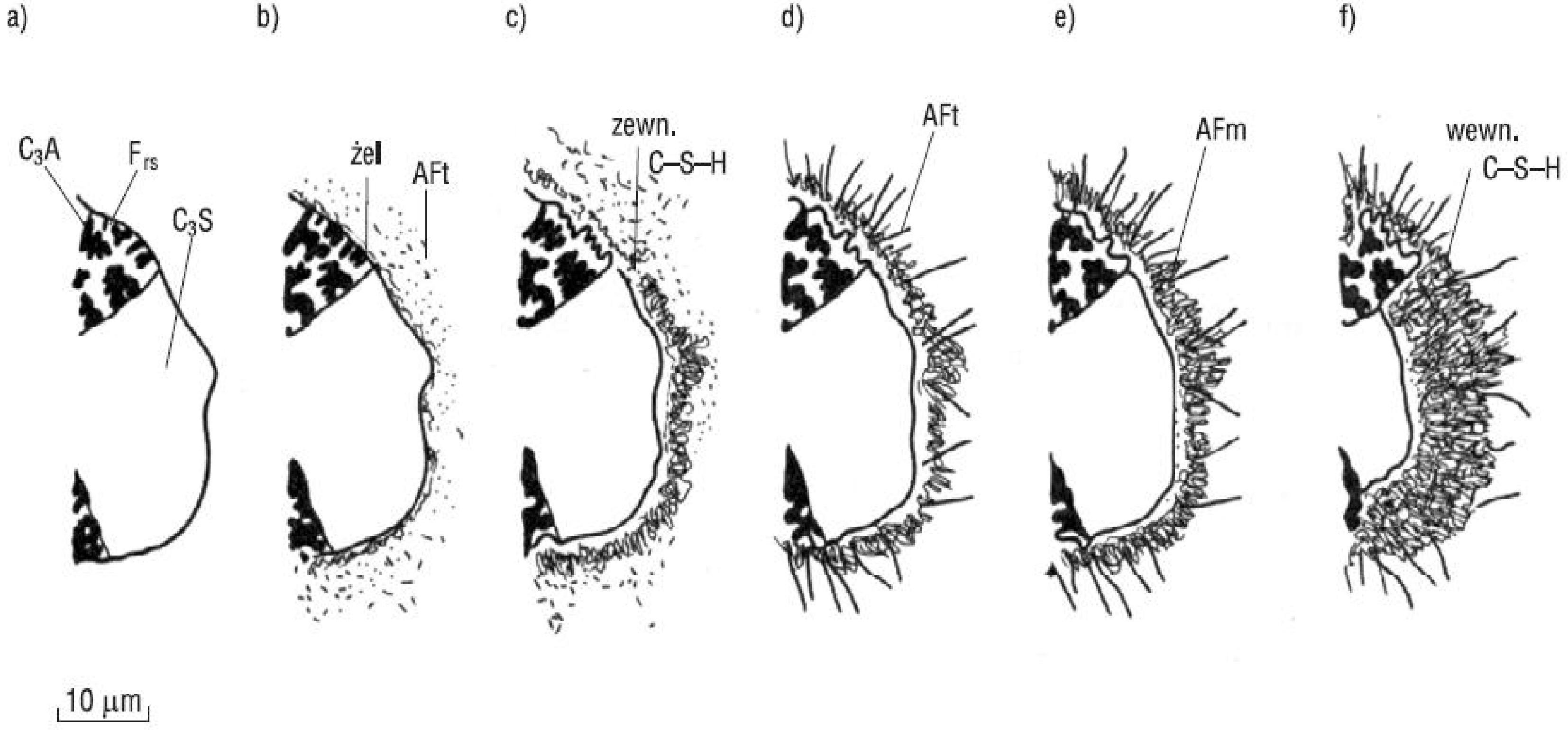
The Troubles with Ettringite Expansion



The Troubles with Ettringite Expansion



The Troubles with Ettringite Expansion

There is an well establish opinion that the ettringite crystallization has the advantageous influence on concrete strength and for this reason the high content of C_3A and high alumina modulus are the very desirable factors for rapid hardening cements

Zn as an accelerator of setting

- Low sulphate ions concentration in pore solution
- Slow ettringite layer formation around C_3A crystals
- Thus very quick „ettringite” cement setting, with Zn about 15 min is possible because $Zn(OH)_2$ hinders this layer formation
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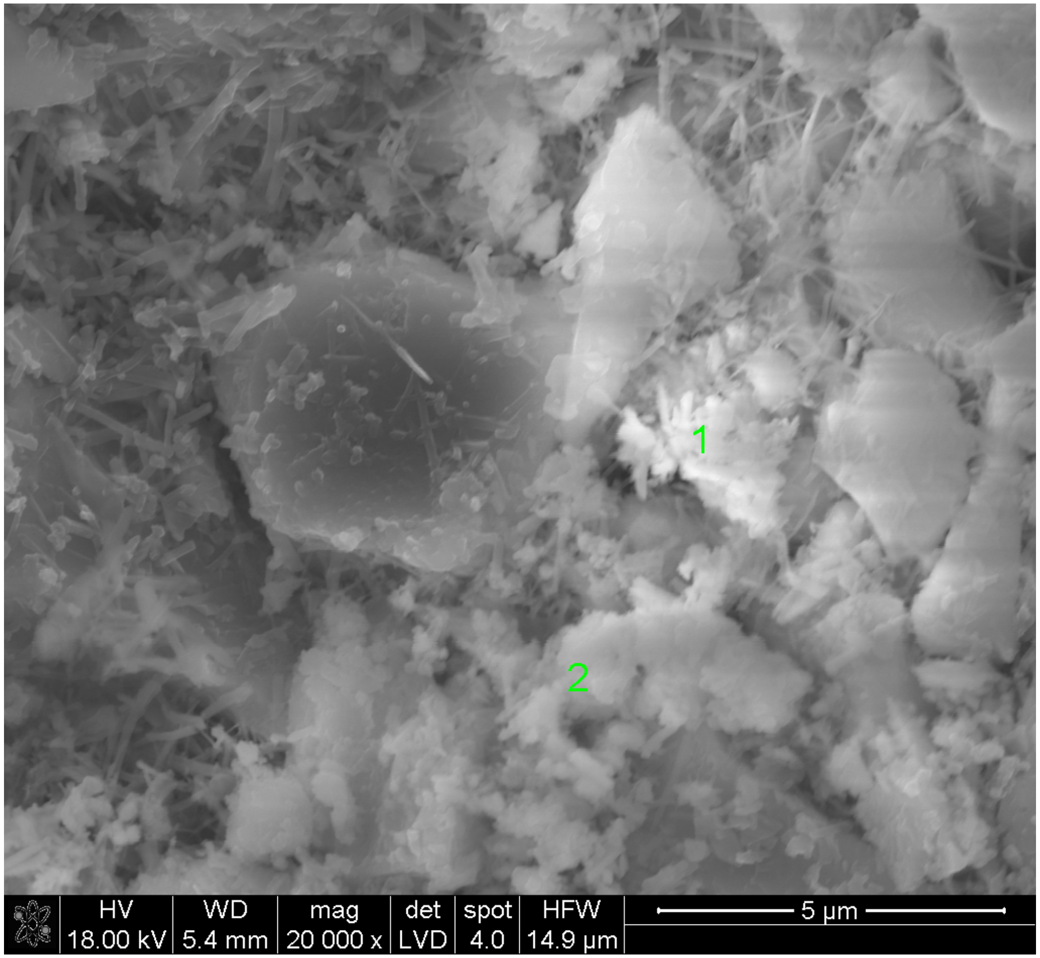
Ettringite setting



„Ettringite” setting

- „Ettringite” setting is a proof that the layer around C_3A is the first process in the reaction of cement with water

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Contraction $CaO + H_2O \rightarrow Ca(OH)_2$

$$\frac{56,08}{3,32} + 18 \rightarrow \frac{74,08}{2,23}$$

$$16,89 + 18 \rightarrow 33,22$$

$$34,89$$

$$\Delta V = 1,67$$

$$\frac{1,67\,cm^3}{56,08} = 2,9\%$$

Free $CaO_{1450}{}^{o}$ in cement → expansion

Explanation:

- Formation „in situ” after cement paste hardening
- CaO surrounded by impermeable layer of gel

only water molecules can enter inside

Volume of CaO < $Ca(OH)_2$

16,89 < 33,22

For ettringite

$$C_3A + 3\left(CaSO_4 \cdot 2H_2O\right) + 26H_2O \rightarrow C_3A + 3CaSO_4 \cdot 32H_2O$$

$$\frac{270.2}{3} + 3 \cdot \frac{172.25}{2.32} + 26 \cdot 18 \rightarrow \frac{1255.13}{1.73}$$

$$780.7\text{cm}^3 \rightarrow 725.5\text{cm}^3$$

Same explanation for ettringite

Volumes:

C_3A – 90.07

3 x gypsum = 222.41

Total = 312,48 → 725.5

Formation „in situ” after cement paste hardening

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Ettringite – friend or foe ? Asked Taylor

Taking into account only solid phases:

$C_3A + 3\ CaSO_4 + 32H_2O \rightarrow$

$C_3A \cdot 3\ CaSO_4 \cdot 32H_2O$

88.88 cm^3 + 137.97 cm^3 = 226.85 → 725.5 cm^3 Increase of volume high 498.65 cm^3 on 1 mole of ettringite = about 69%.

Taylor C-S-H = 52 cm^3/ mole of C_3S =118% and no expansion !!

Ettringite expansion

- Several hypothesis:
- Lafuma = topochemical reaction
- Mehta = water absorption
- Crystallization pressure

The last one was adopted during the International RILEM TC 186-ISA Workshop on „Delayed Ettringite Formation”

Internal sulphate corrosion

Alcali silica reaction

Delayed Ettringite Formation

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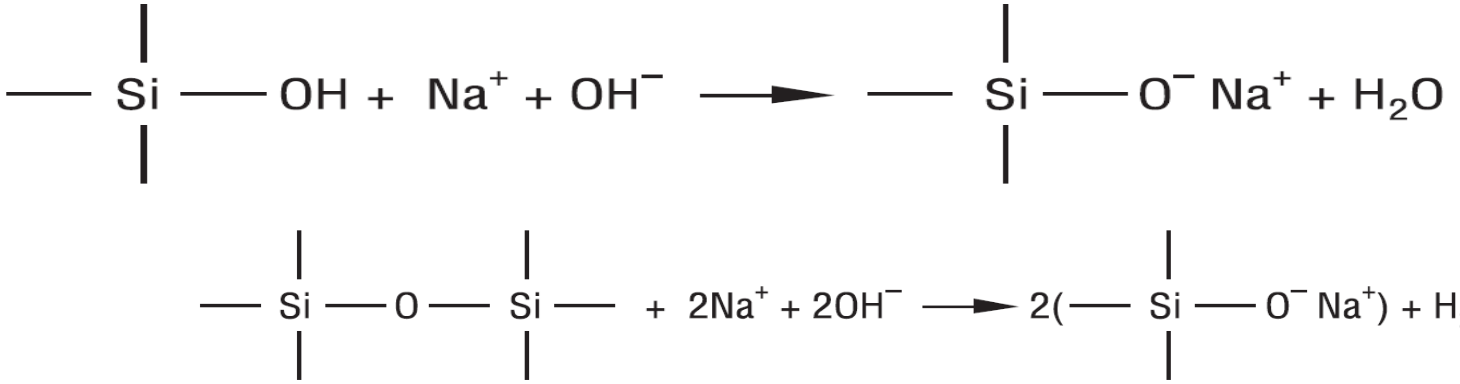
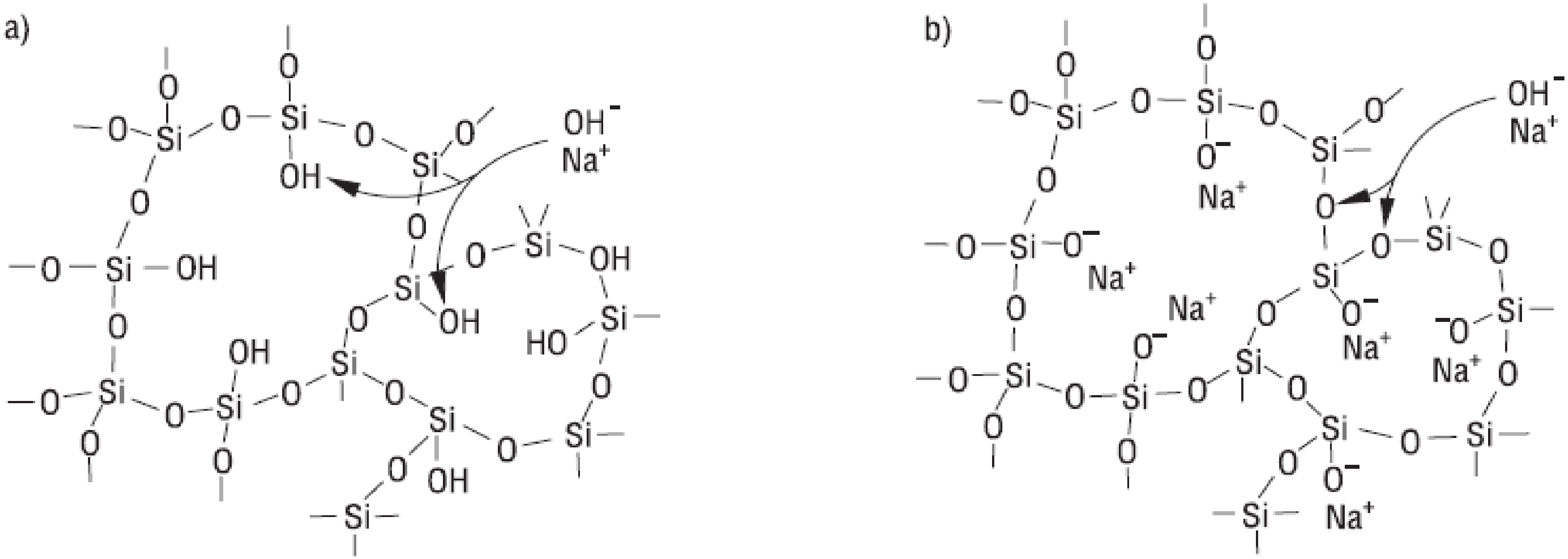
Alcali silica reaction

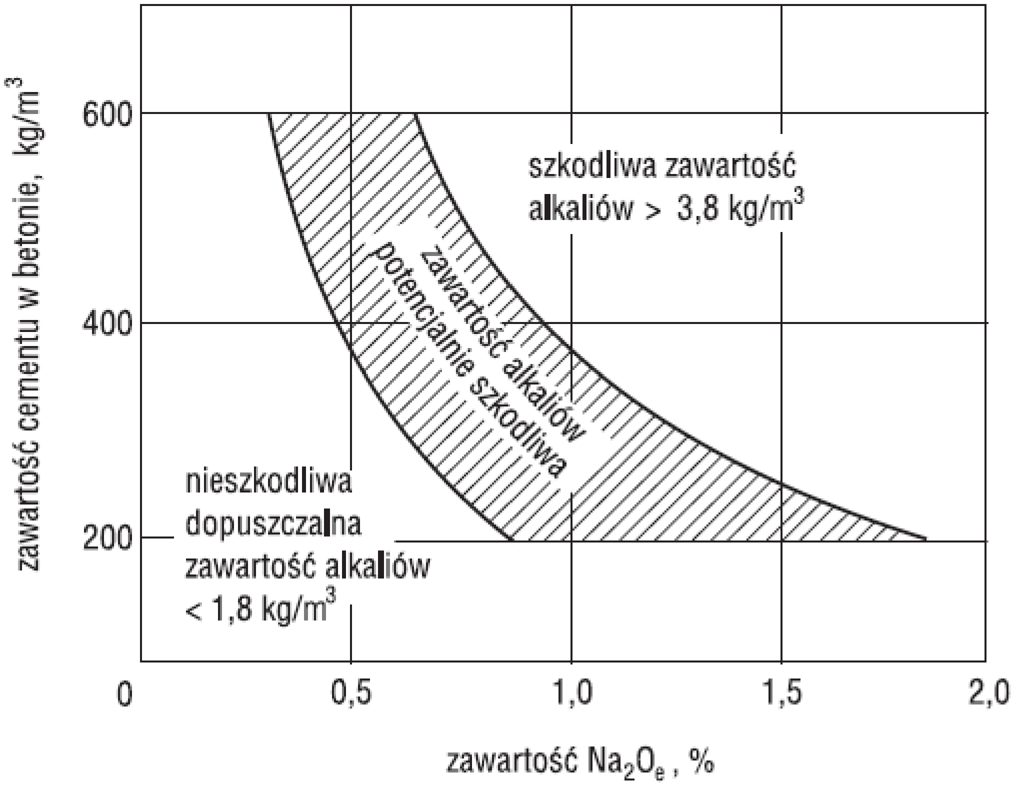


$$-\mathrm{Si}-\mathrm{OH} + \mathrm{Na}^+ + \mathrm{OH}^- \longrightarrow -\mathrm{Si}-\mathrm{O}^-\,\mathrm{Na}^+ + \mathrm{H_2O}$$

$$-\mathrm{Si}-\mathrm{O}-\mathrm{Si}- + 2\mathrm{Na}^+ + 2\mathrm{OH}^- \longrightarrow 2(-\mathrm{Si}-\mathrm{O}^-\,\mathrm{Na}^+) + \mathrm{H_2O}$$



Alcali silica reaction

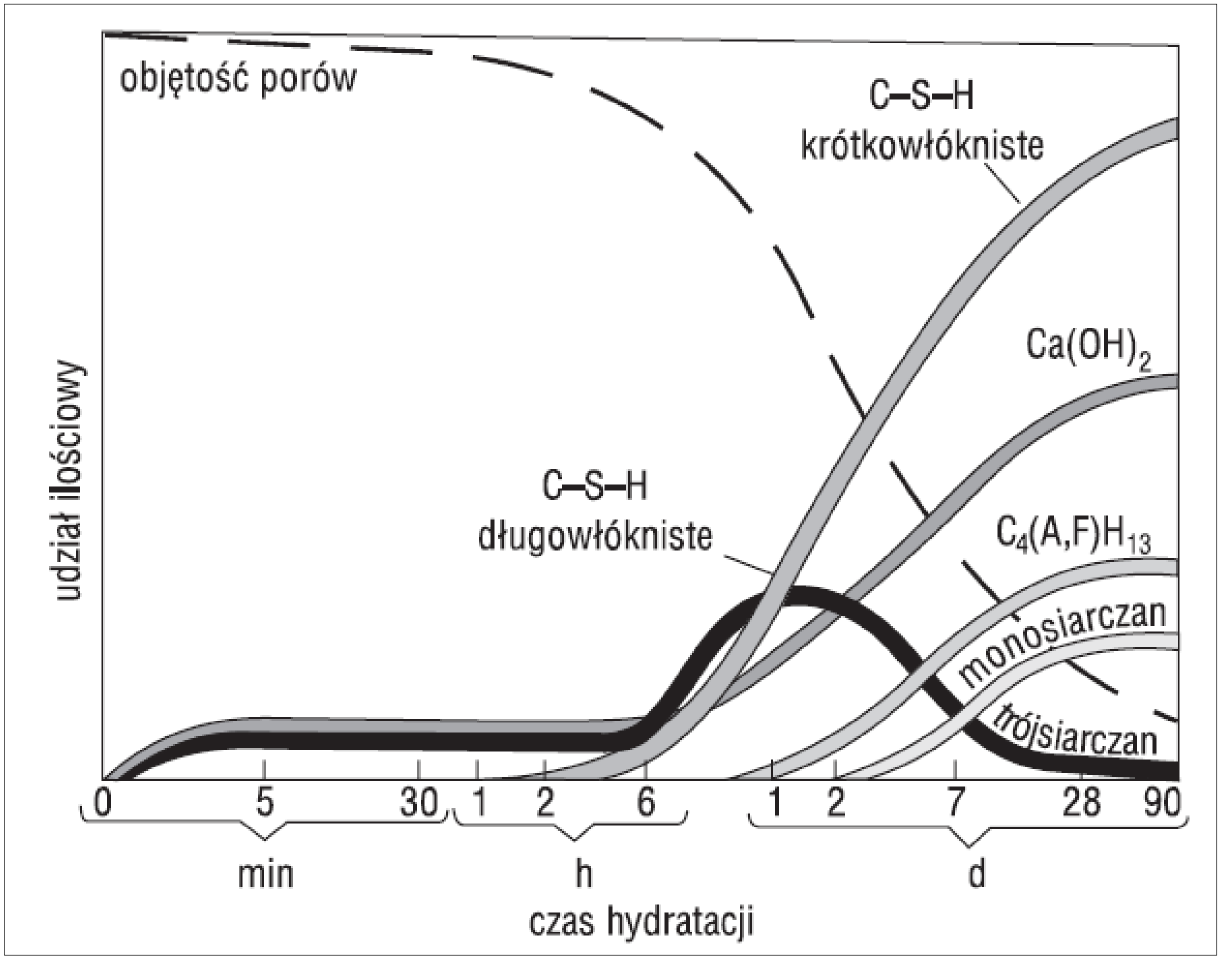


Ettringite at normal temperature

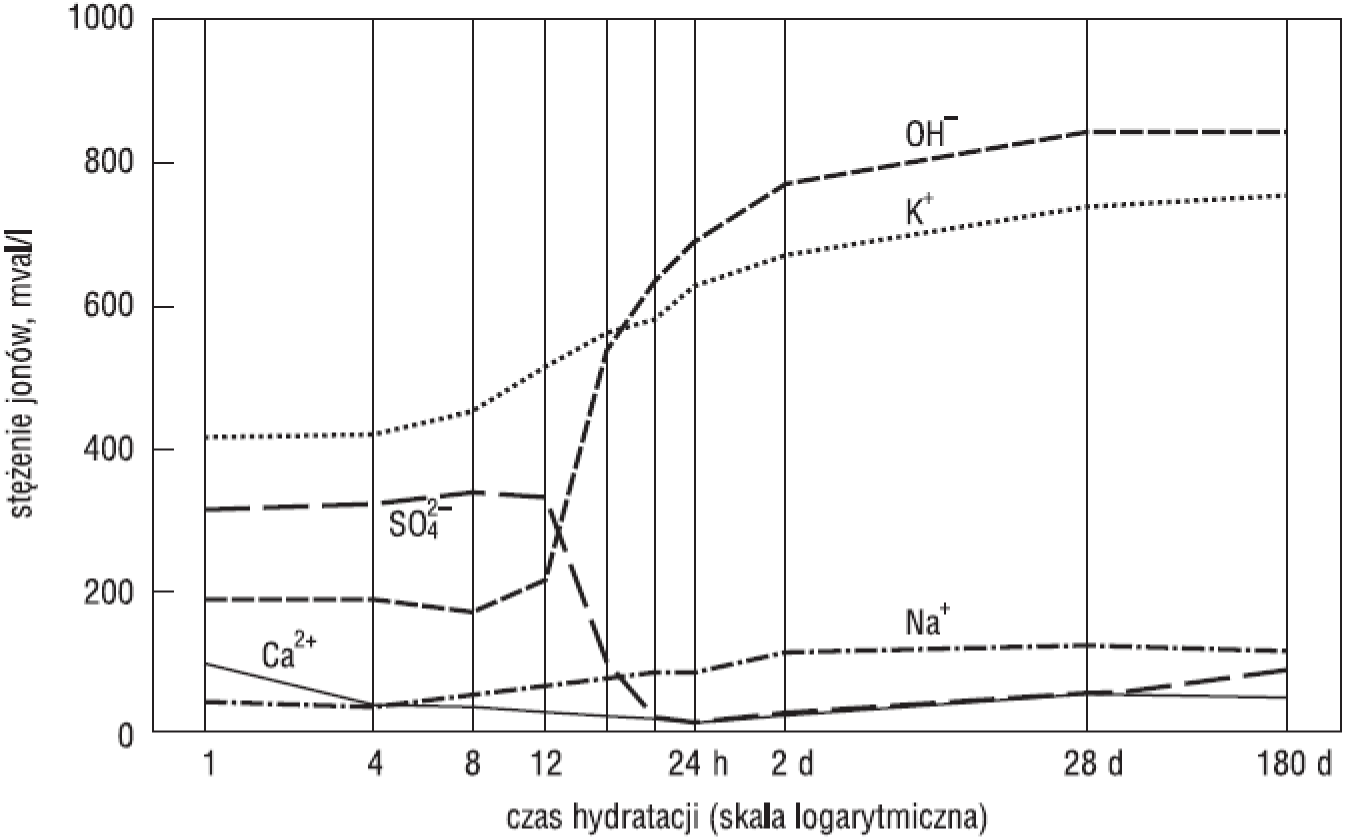
During the concrete hardening at normal temperature ettringite is formed in the period of 24 h -30 h

Concrete is then plastic and the plastic deformations are neutralizing the stresses caused by ettringite crystallization

Ettringite at 20^{o}C



Paste solution at 20^{o}C

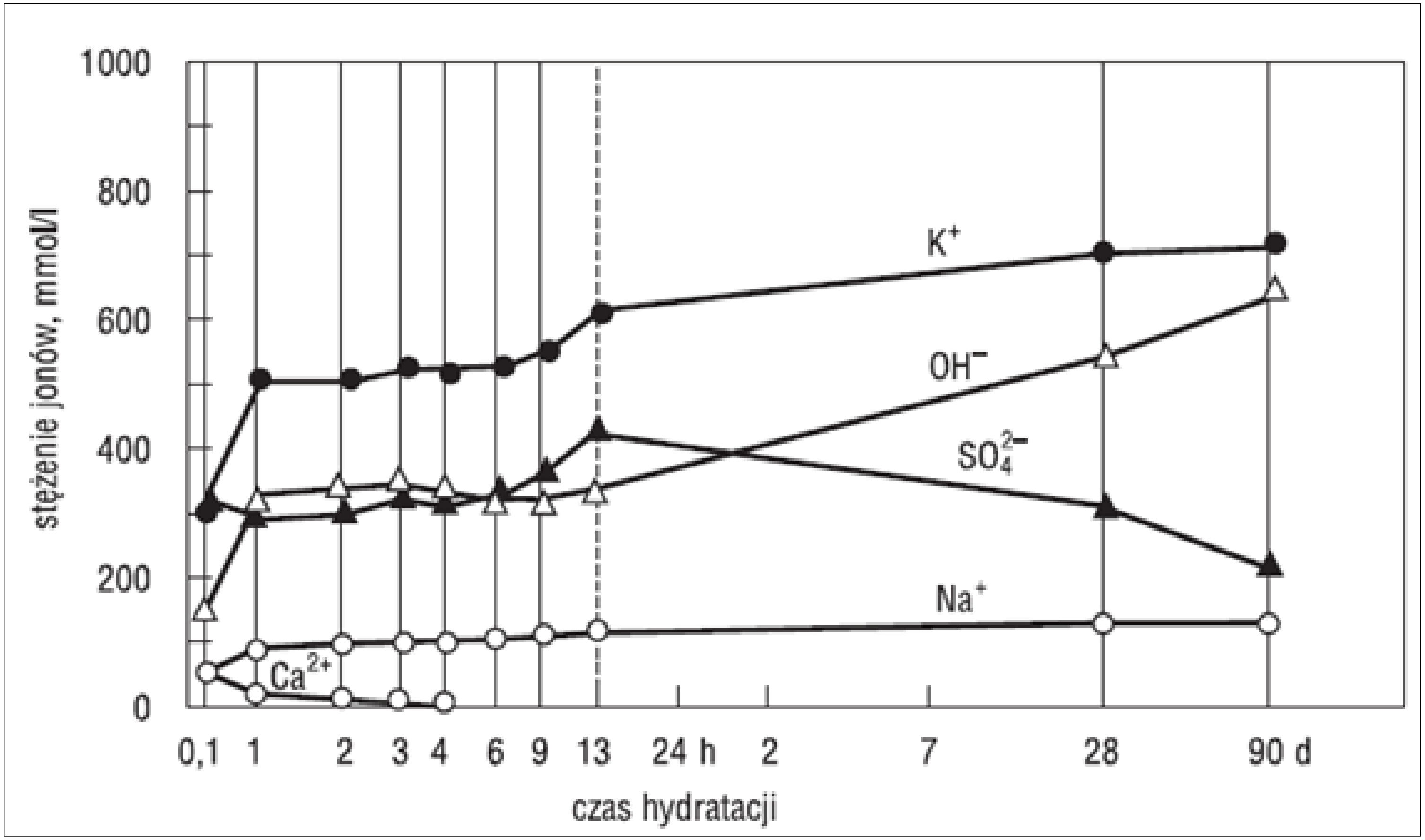


DEF

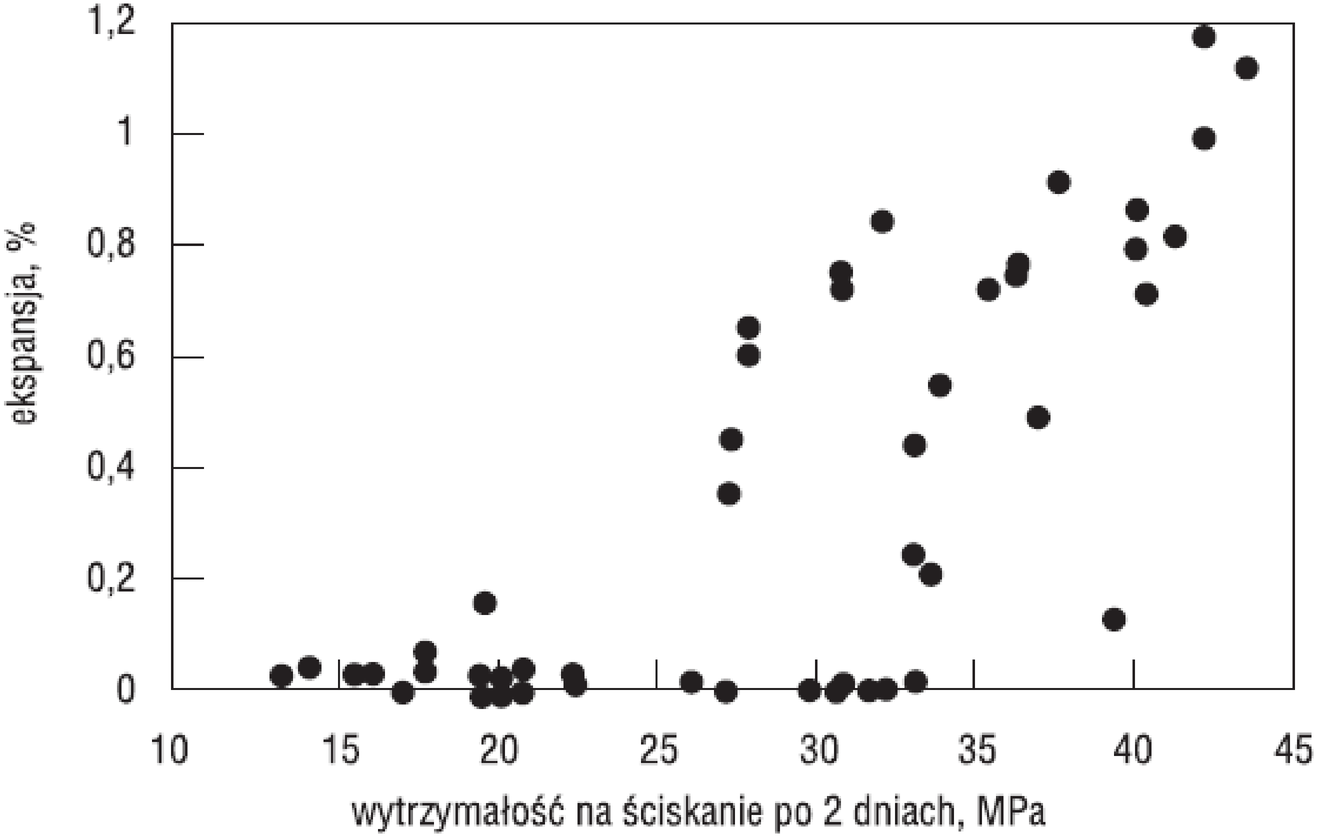
The destruction of concrete sleepers due to delayed ettringite formation was detected for the first time in Germany by Ludwig and Heinz in early eighties.

Wieker has established that when in cement paste solution the concentration of NaOH is higher than 400 mmoles/L ettringite is not stable when the temperature of concrete heat treatment is higher then 70^{o}C.

DEF


1000
800
600
400
200
0
stężenie jonów, mmol/l
K+
OH−
SO42−
Na+
Ca2+
0,1
1
2
3
4
6
9
13
24 h
2
7
28
90 d
czas hydratacji

DEF

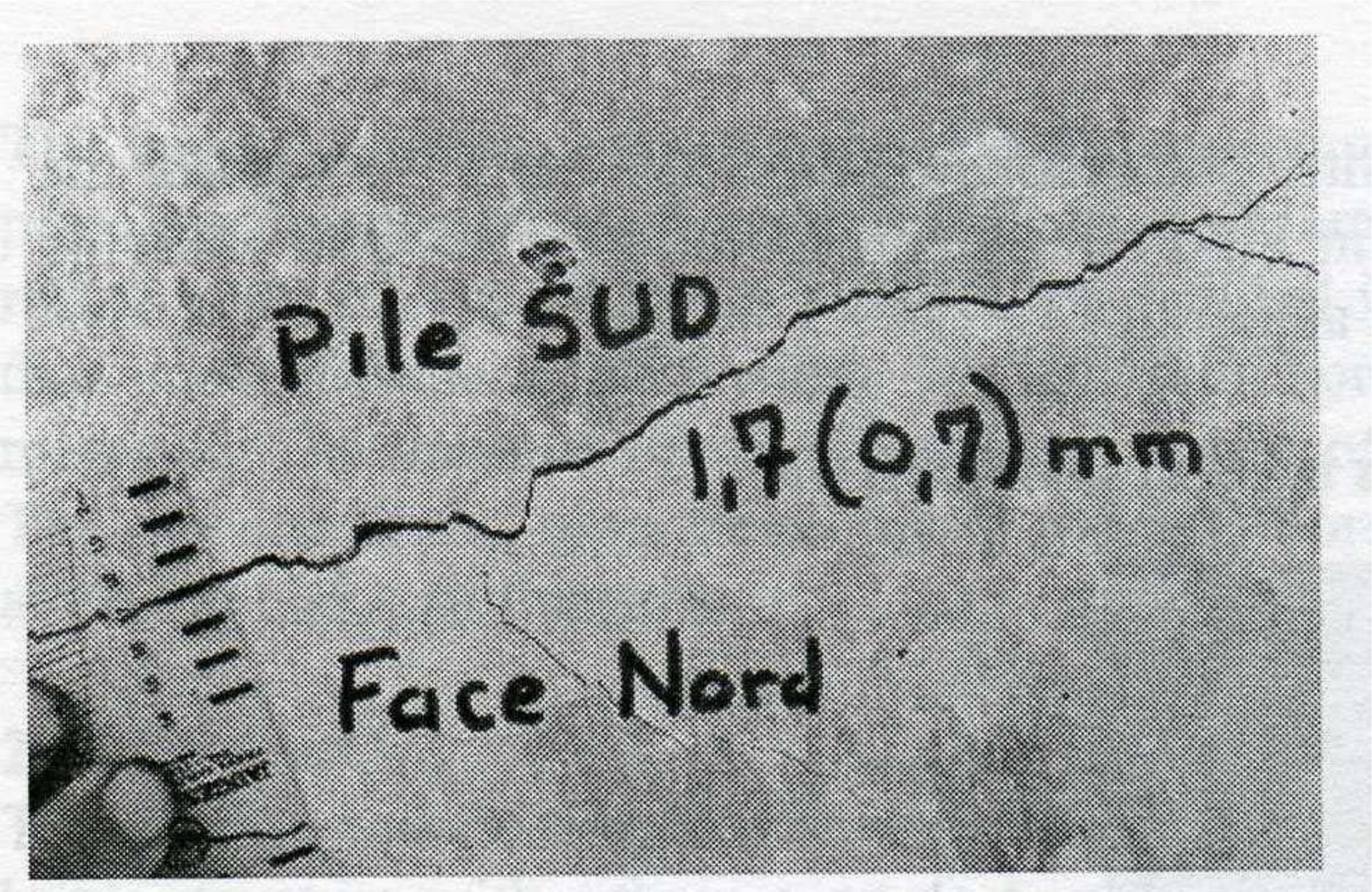

1,2
1
0,8
0,6
0,4
0,2
0
ekspansja, %
10
15
20
25
30
35
40
45
wytrzymałość na ściskanie po 2 dniach, MPa

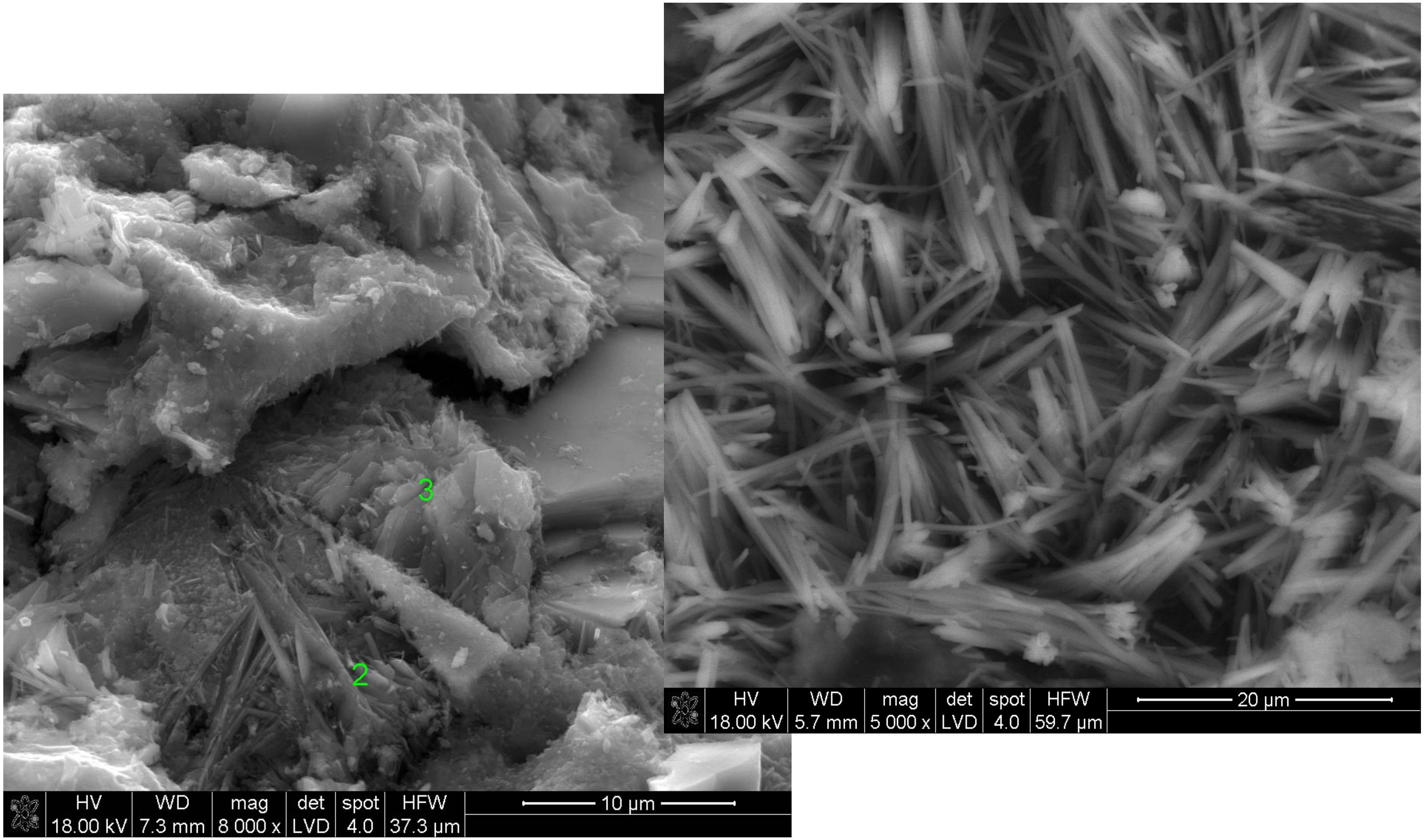
DEF

In cement there is about 0,8% K_2O equal to 1,8% K_2SO_4, which in reaction with $Ca(OH)_2$ gives 340 mmoles KOH and 170 mmoles/L for w/c = 0,5; but for w/c = 0,35 it will be 486 mmoles KOH and 243 mmoles/L of SO_4^{2-} . The concentration is increasing with w/c decrease.

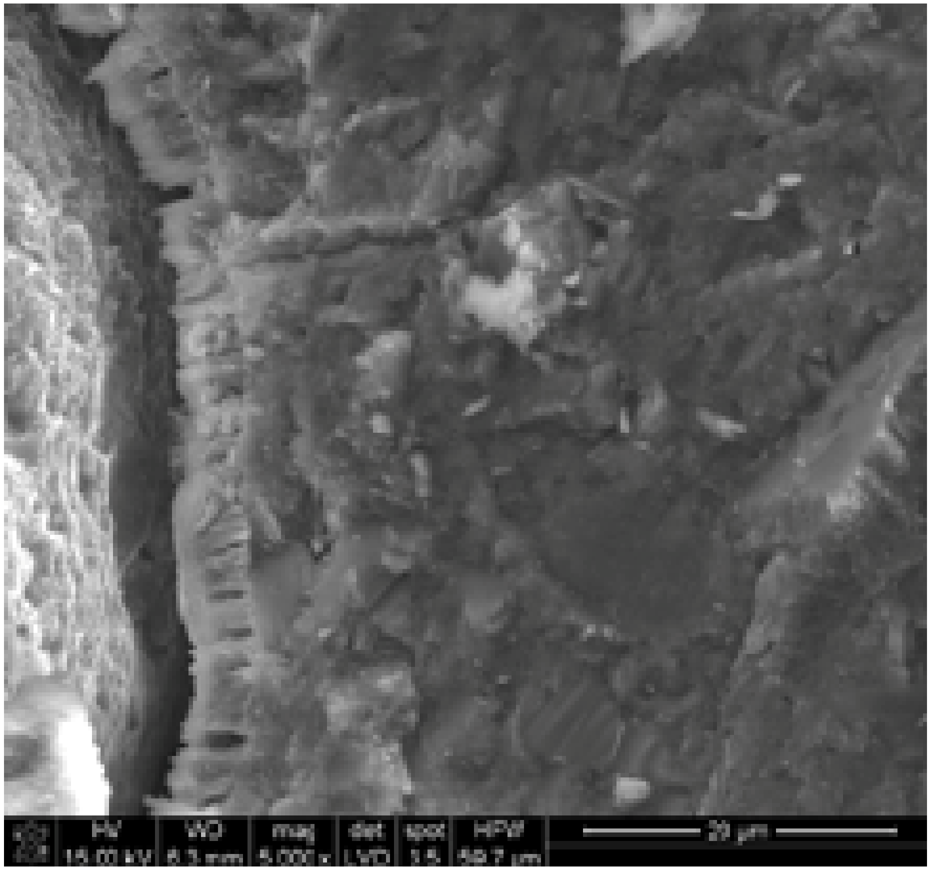
Important $Na_2O_e < 0,6\%$

DEF in bridge support




3
2
HV 18.00 kV
WD 7.3 mm
mag 8 000 x
det LVD
spot 4.0
HFW 37.3 µm
10 µm
HV 18.00 kV
WD 5.7 mm
mag 5 000 x
det LVD
spot 4.0
HFW 59.7 µm
20 µm

Massive ettringite layer around sand grain



Massive ettringite

- Diamond presented the opinion contrary to previously described that massive ettringite is also causing expansion. Similarly as portlandite deposits on sand grains ettringite can crystallize and generate expansive forces. The degree of supersaturation required is much smaller for this heterogeneous nucleation.
- I agree with this opinion.
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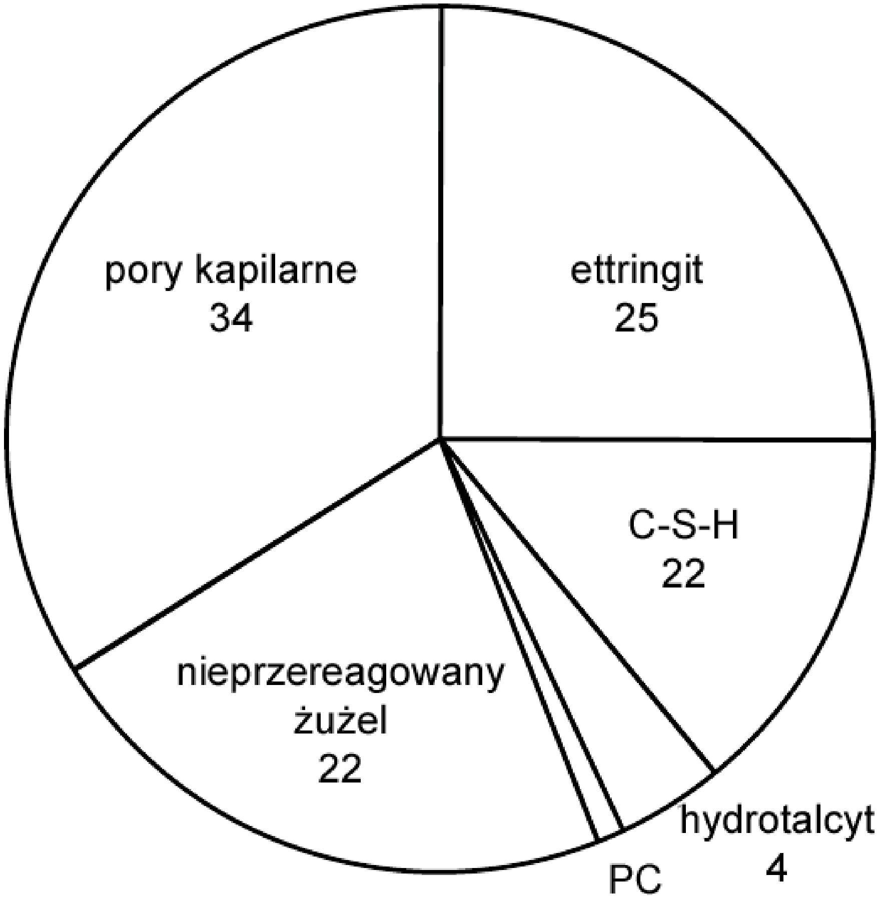
Ettringite – friend or foe ? Asked Taylor

There are special cements:
„supersulphated slag cement”
„belite sulphoaluminate cement”
During hydration of these cements
high content of ettringite is formed

Special cements

In these cements ettringite is formed much longer than in Portland cement, thus after concrete hardening and is one of its main components assuring high strength of concrete produced of these cements

Paste of supersulphated slag cement, 3 d.



Concrete of supersulphated slag cement

The dam in South Africa in Beervlei constructed in 1954 – 1956 period , the concrete samples taken by Gebauer in 2000 year had the strength of 124 MPa Cement matrix was composed of small ettringite crystals surrounded by gel composed of $Al(OH)_3$ + C-S-H

Taylor’s explanation

Taylor put attention on the role of calcium hydroxide in the process of ettringite crystallization.

This hypothesis was proposed independently Okushima and Nakamura

Taylor’s explanation

$Al(OH)_4^-$ ions concentration in pore solution is very low. However, if the Ca^{2+}, SO_4^{2-} ions concentration will be high, in this condition the divusion of $Al(OH)_4^-$ ions will be not far from their source i.e. C_3A crystals and ettringite crystallization will be concentrated in this small volume.

Taylor’s explanation

Then the crystals growth will produce high stresses and expansion.
Taylor is stating that , in the case of low $Ca(OH)_2$ concentration , the diffusion of $Al(OH)_4^-$ ions will be free in the solution.
In this condition ettringite crystals will be dispersed in the cement paste and the oversaturation will be low thus also a stress produced by ettringite crystals growth will be low

Taylor’s explanation

The same explanation can be given for concrete of supersulphated slag cement studied by Gebauer in Breevlei dam. This cement was elaborated by Kùhl in 1908 year and is composed of slag (80-85%) with high anhydrite II addition (10-15%) and low Portland cement content (= 5%). In the paste of this cement high content of ettringite is formed, however, there is no expansion because the oversaturation with $Ca(OH)_2$ in pore solution is low.

Summary and conclusions

The discussed problems can be summarized as follows.
The internal expansion caused by ASR and DEF can be avoided if the sodium and potassium content will be under control. For ASR Na_2O_e content should be lower than 180 kg/m^3 of concrete.

Summary and conclusions

For DEF Na_2O_e concentration should be lower than 400 mmoles/L if the expected temperature of concrete should be higher than 70^oC.

Ettringite will be not producing the harmful expansion if the oversaturation of $Ca(OH)_2$ will be low

Final remarques

All the conclusions are limited to the cement only and do not take into account the disadvantageous components in aggregates, which should be also carefully examined in the case of any doubts.

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Ettringite is a friend !

Thank You for your attention !!