Investigation of C_3S early hydration by Environmental Scanning Electron Microscope (ESEM)

Sakalli, Y.; Trettin. R.: Journal of Microscopy, Vol. 259, Issue 1 2015, pp. 53–58
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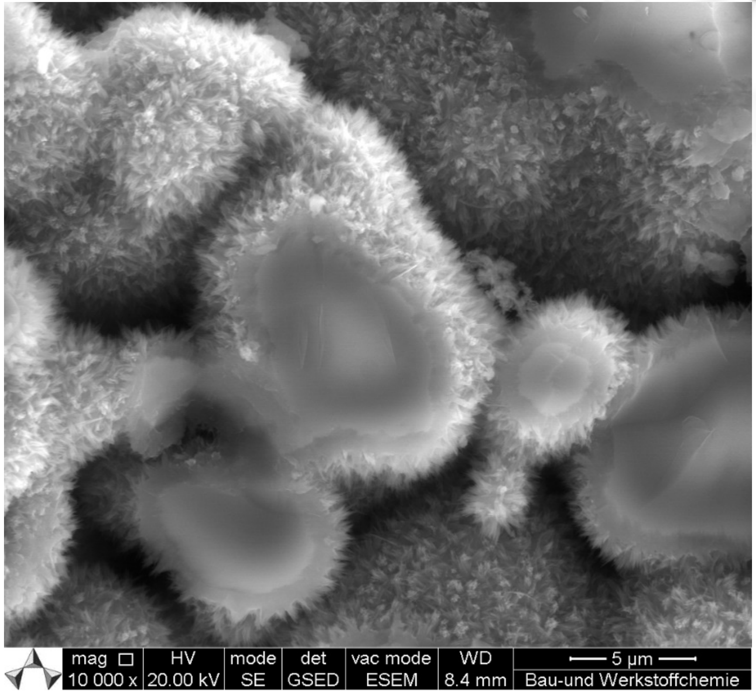

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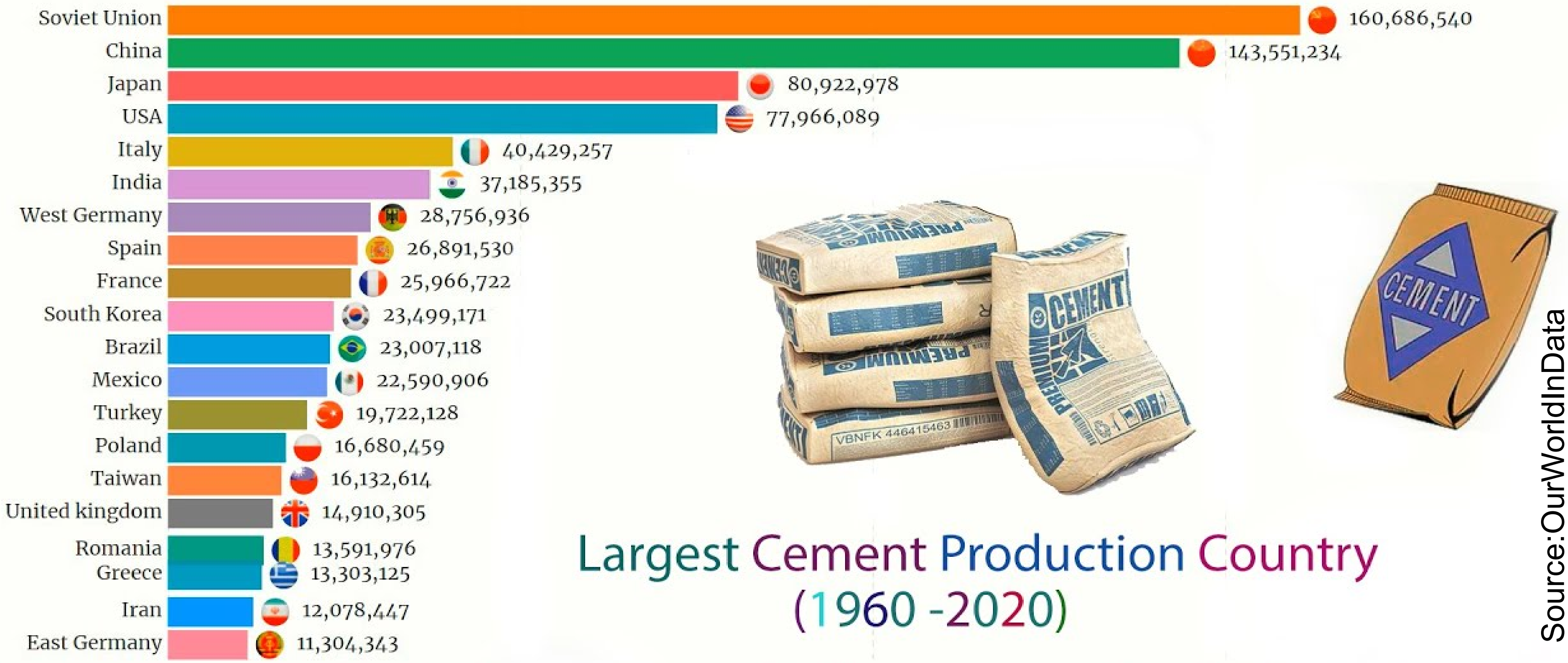
Top 20 Cement producing Countries

1960 -2020(Metric Tonnes)



Largest Cement Production Country

(1960 -2020)

Source:OurWorldInData

China produces the most cement globally by a large margin, at an estimated 2.2 billion metric tons in 2019, followed by India at 320 million metric tons in the same year. China currently produces over half of the world's cement. Global cement production is expected to increase from 3.27 billion metric tons in 2010 to 4.83 billion metric tonnes in2030.

Motivation

- **Why C_3S Hydration?**

  Alite is the major component of the Portland cement clinker. The exact mechanism of the hydration of C_3S has not been elucidated. However, there are models that were derived based on experimental observations of hydration.

- Why ESEM?

  The special work mechanism of ESEM allowed us the investigation of inorganic binder without treatment.

Introduction

- Portland cement composes of four different main clinker phases: Alite (C_3S), Belit (C_2S); Aluminate (C_3A) and Ferrite (C_4AF)
- C_3S and C_2S are mainly responsible for the strength of the hardened concrete
- C_3A and C_4AF are needed for the reaction in rotary kiln
- C_3S reacts faster then C_2S

C = CaO, A = Al_2O_3, S = SiO_2, F = Fe_2O_3, T =TiO_2,

M = MgO, N = Na_2O, K = K_2O, H = H_2O, s or S= SO_3

Introduction

Reason for high pH → protection of steel reinforcement

Hydration of Alite (C_3S)

$$C_3S + (3 - x + y)\,H \rightarrow C_xSH_y + (3 - x)\,CH$$

Hydration of Belite (C_2S)

$$C_2S + (2 - x + y)\,H \rightarrow C_xSH_y + (2 - x)\,CH$$

Pozzolanic reaction

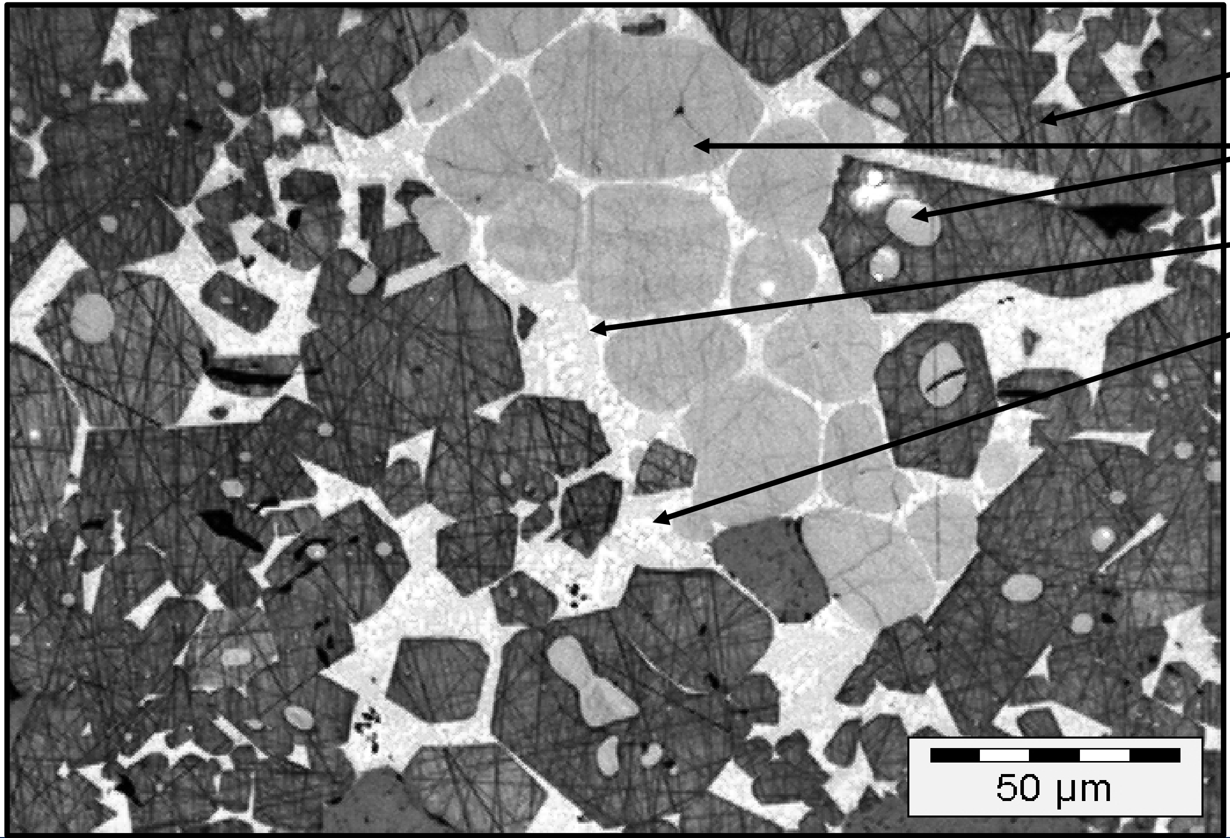
$$CH + S + 2{,}8H \rightarrow CSH_{3,8}$$

C = CaO, A = Al_2O_3, S = SiO_2, F = Fe_2O_3, T = TiO_2,
M = MgO, N = Na_2O, K = K_2O, H = H_2O, s or S= SO_3

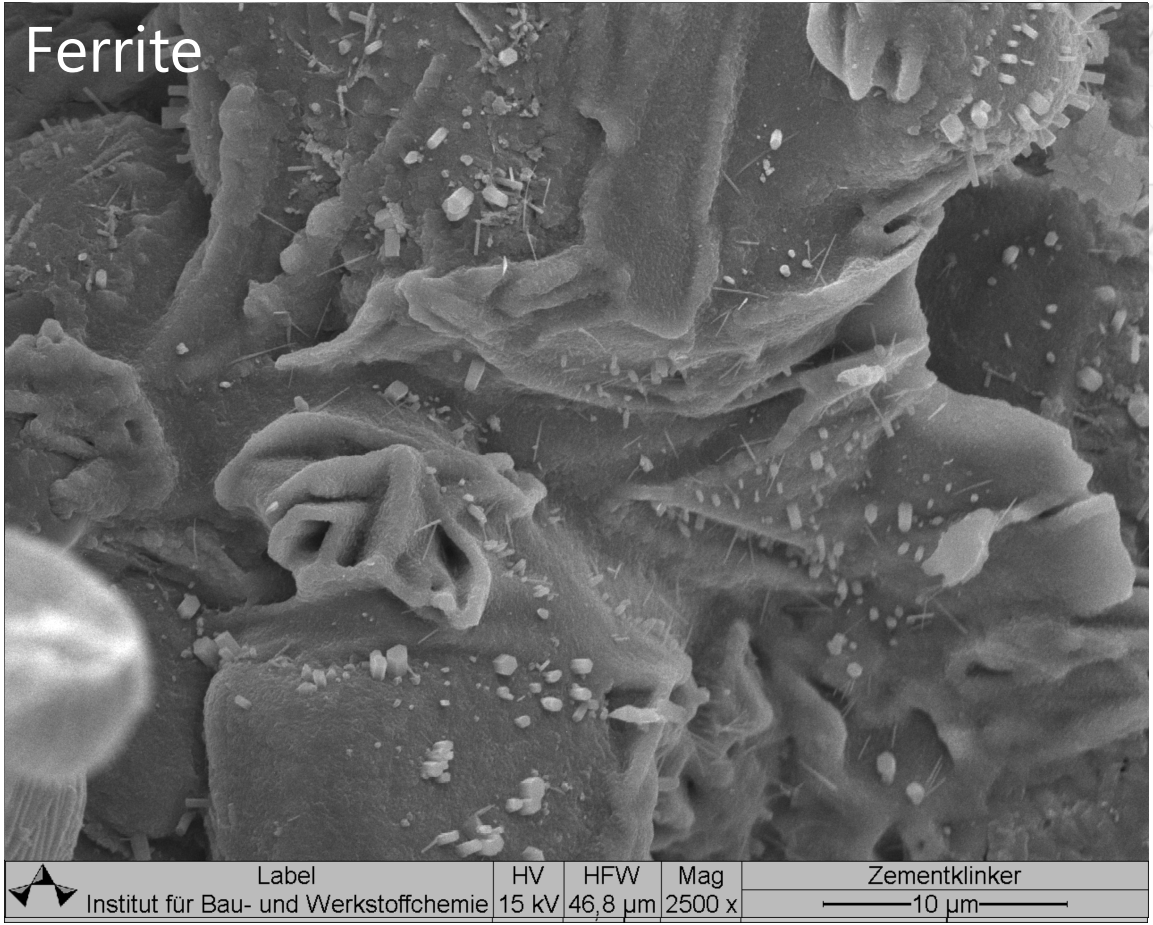
non-ground cement clinker

Introduction

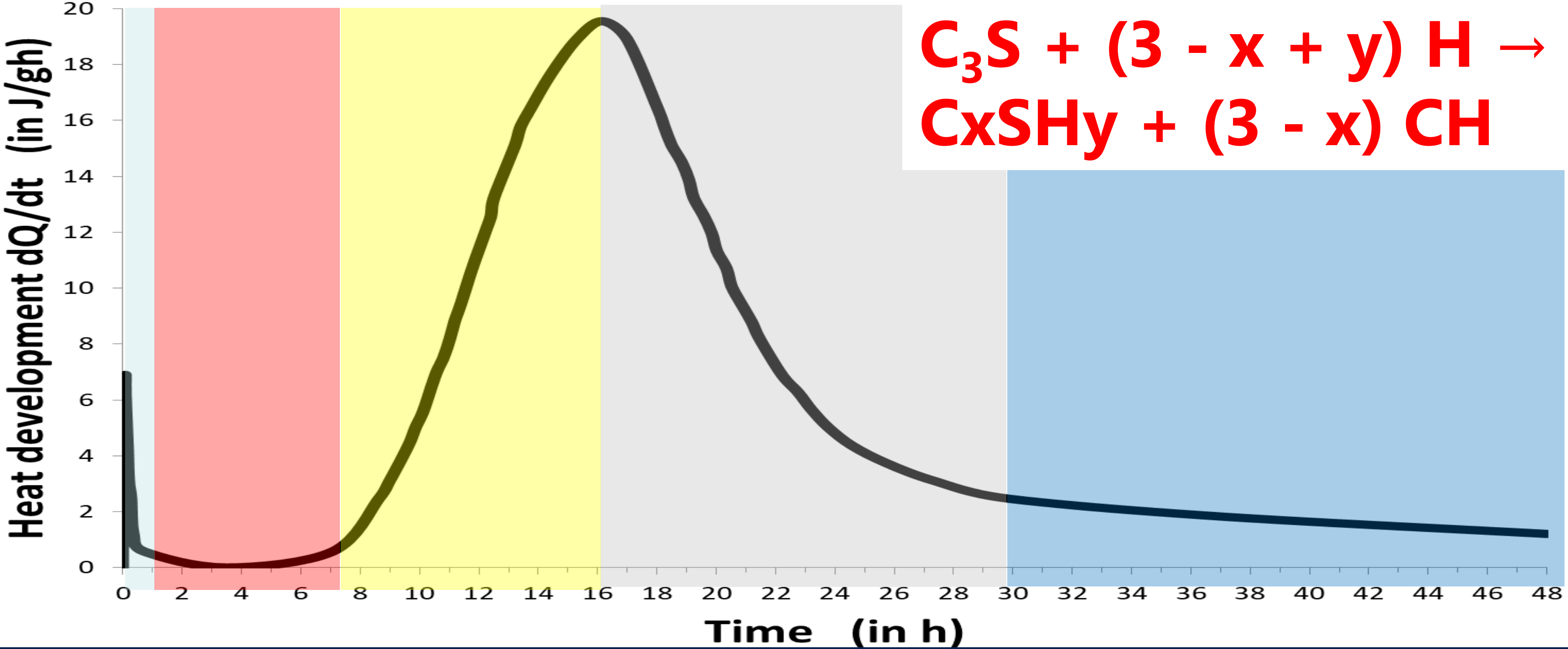
Optical microscopy of Portland cement clinker phases edged with water



EM of Portland cement clinker phases



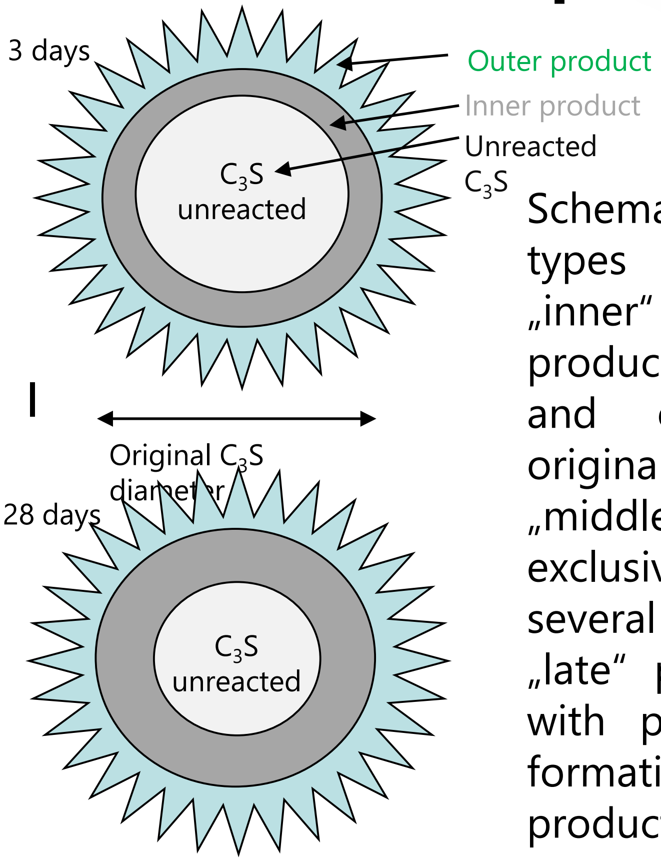
Hydration of C_3S



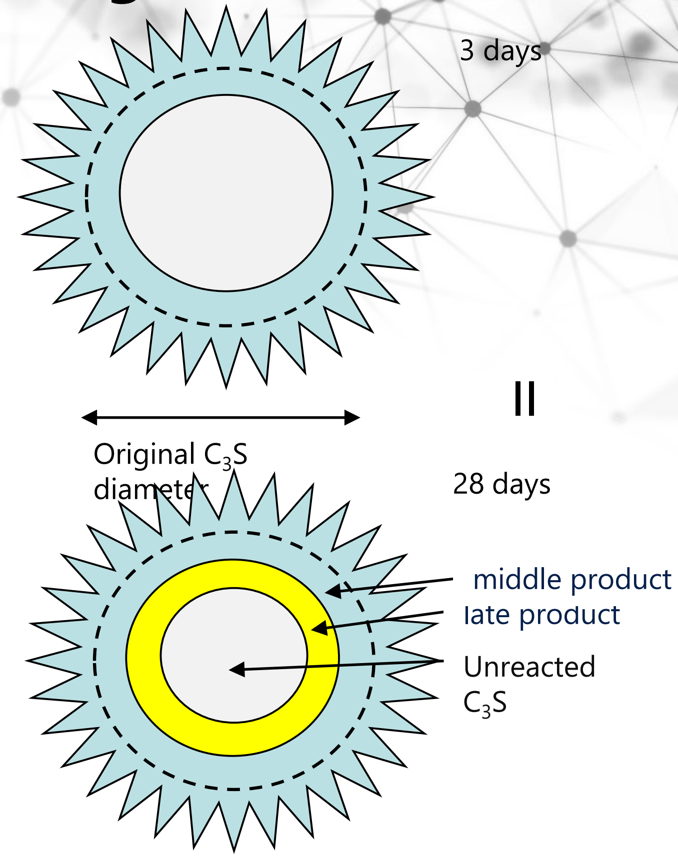
$C_3S + (3 - x + y)\ H \rightarrow CxSHy + (3 - x)\ CH$

I-Pre-induction period (minutes) II-Induction period (hours) III-Acceleration period (hours) IV-Deceleration (hours) V-Slow continuous reaction (days-years)

“Inner" and "outer" product by (Jennings & Parrot, 1986)

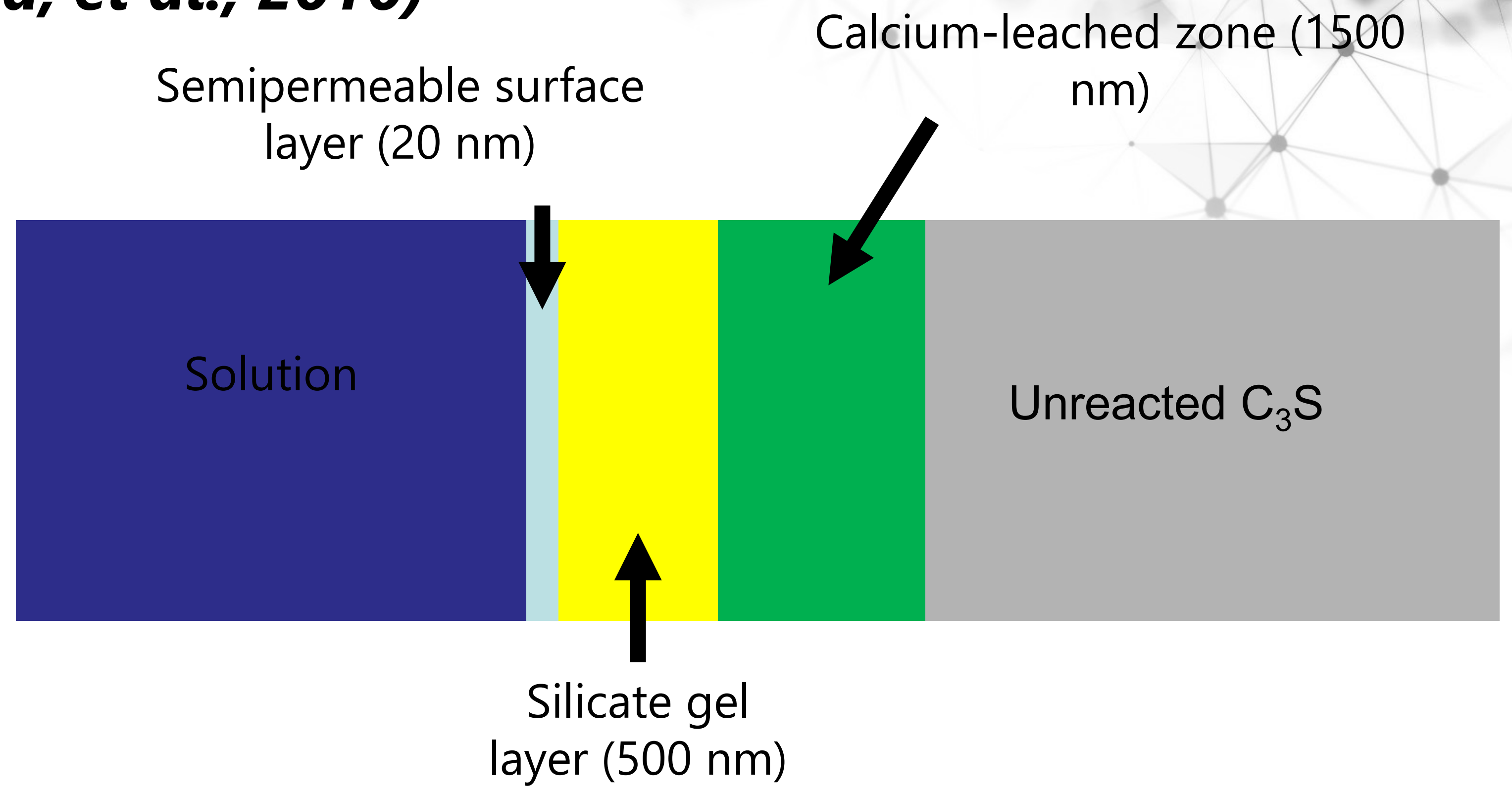


Schematic sketch of two types of hydration: I) „inner“ and „outer“ products forming inside and outside of the original C_3S particle. II) „middle“ product forms exclusively for the first several days followed by „late“ product formation with possibly continued formation of middle product.” Jennings et al.



Jennings, H.M. & Parrot, L.J. (1986) Microstructural analysis of hydrated alite paste. J. Mater. Sci. 21, 4053–4059

NRRA *(Nuclear resonance reaction analysis)* ***Based Model (Bullard, et al., 2010)***



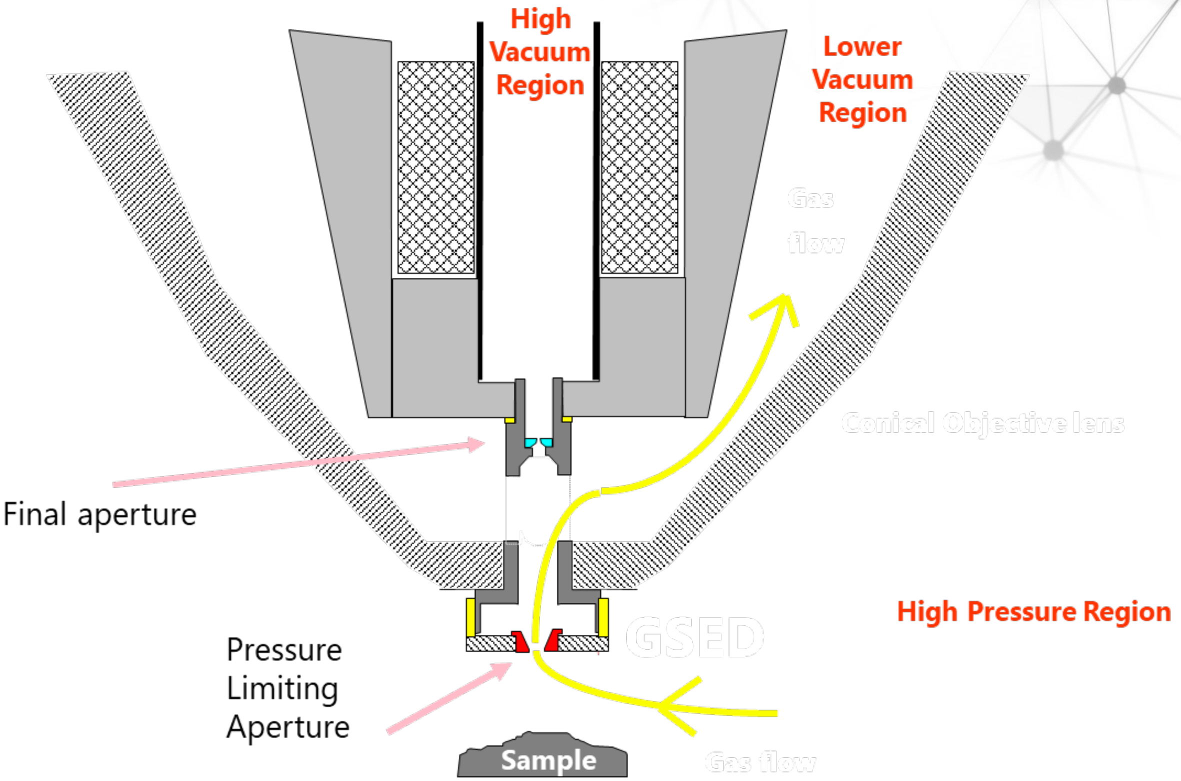
Bullard, J.W., Jennings, H.M., Livingston, et al. (2010) Mechanism of cement hydration. Cement Concrete Res. 41, 1208–1223

SEM vs. ESEM

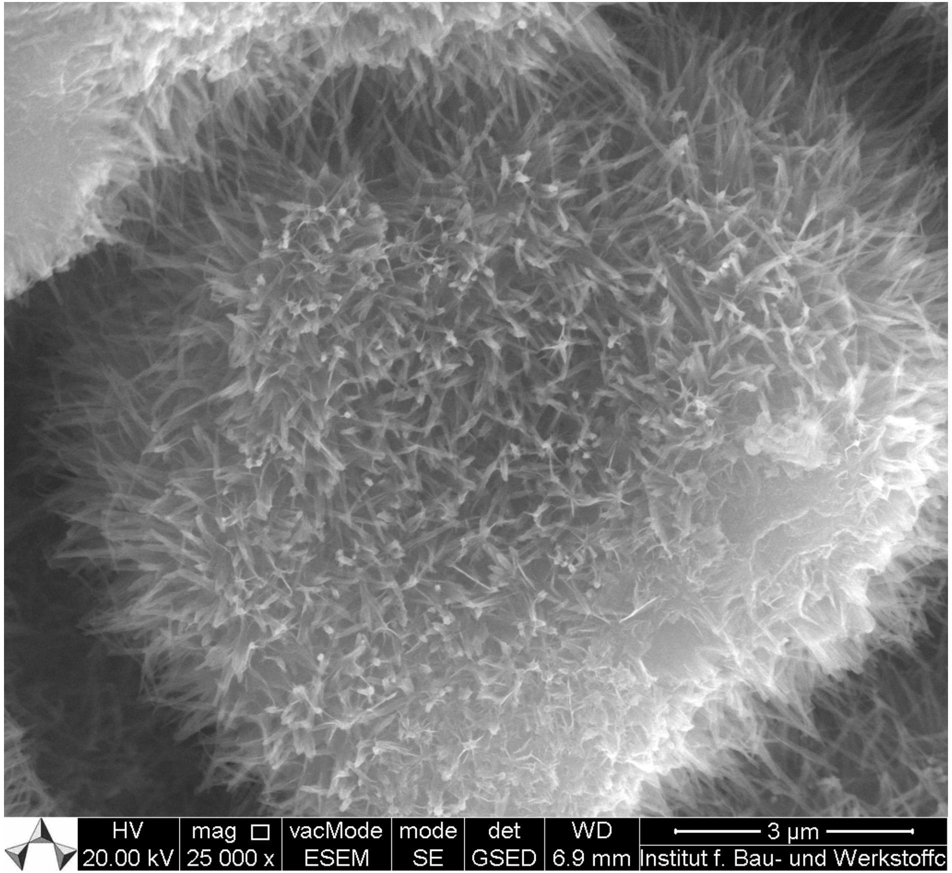
- Scanning Electron Microscope (SEM) is a powerful research tool, but it requires high vacuum conditions.
- The moist and biological samples must undergo a complex preparation that limits the application of SEM on these specimens and often causes the introduction of artifacts.
- The Environmental Scanning Electron Microscopy (ESEM) working in gaseous atmosphere enables high resolution dynamic observations of structure of materials, from micrometer to nanometer scale. This provides a new perspective in material research.

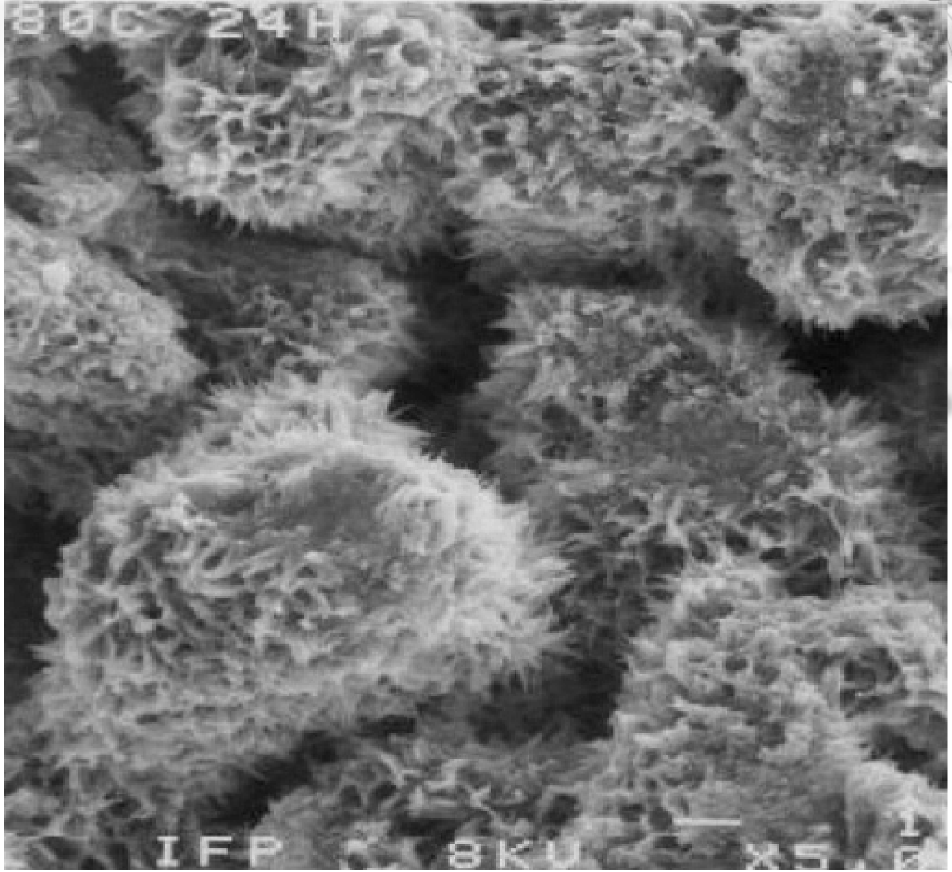
ESEM

Three zone vacuum system



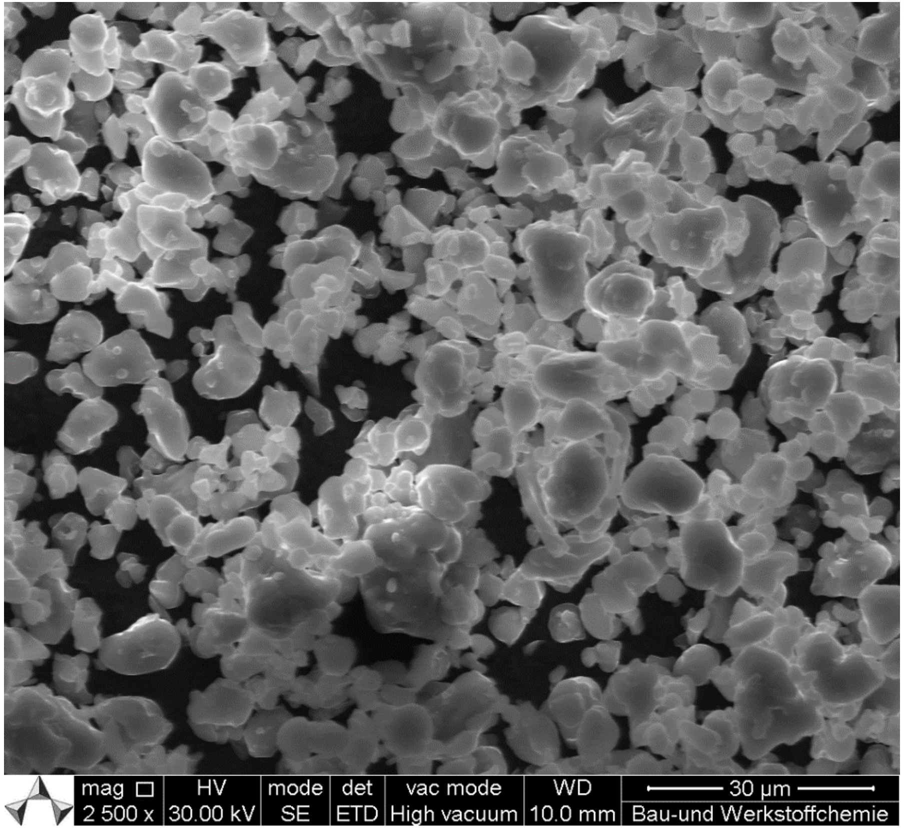
ESEM vs. REM

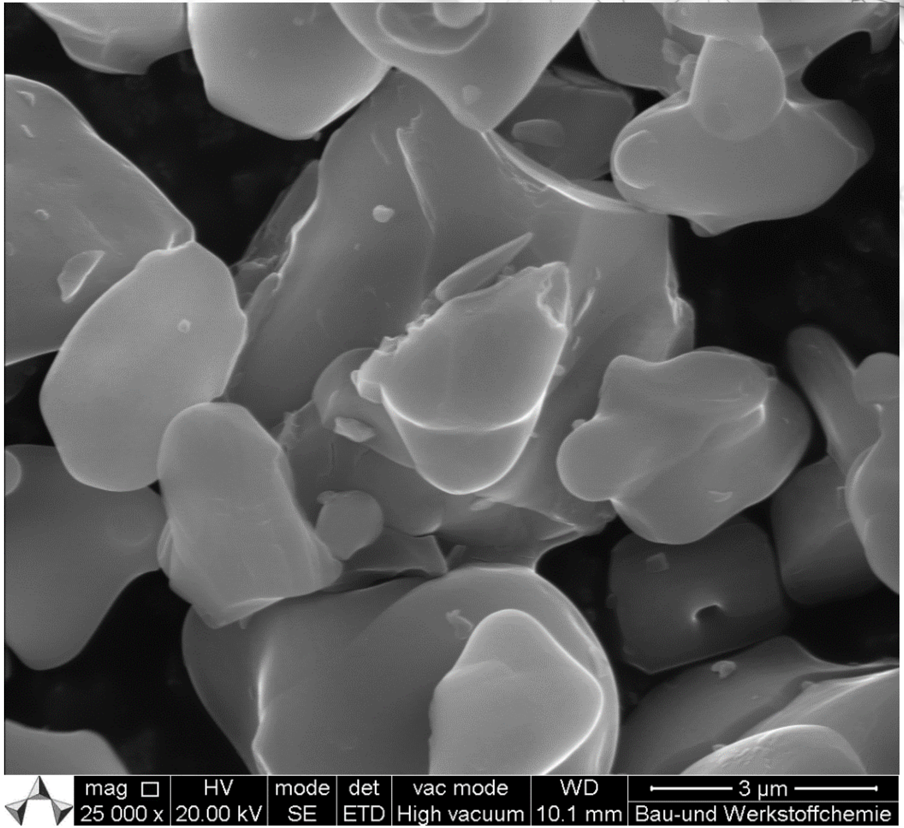




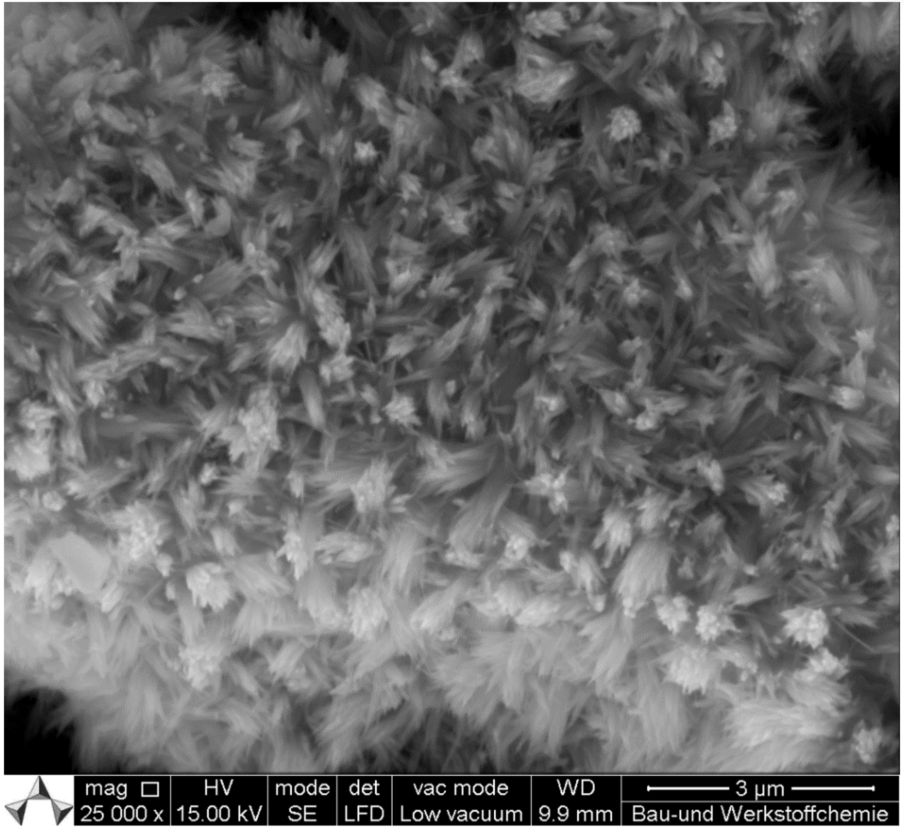
C-S-H (Calcium Silicate Hydrate)

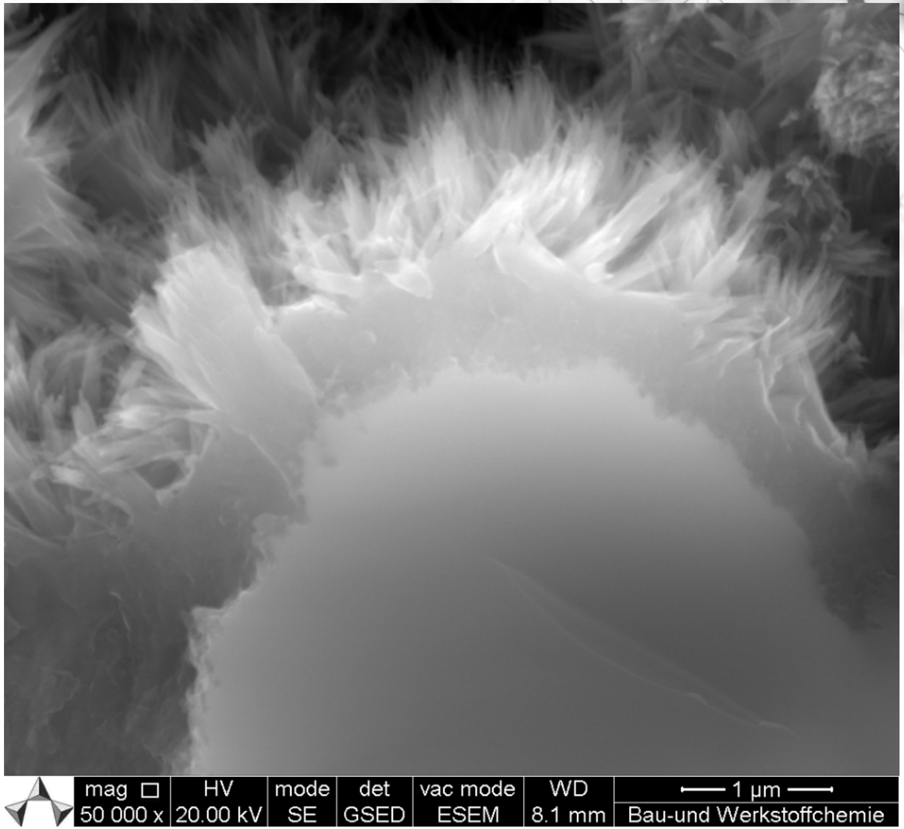
Results C_3S grain pure



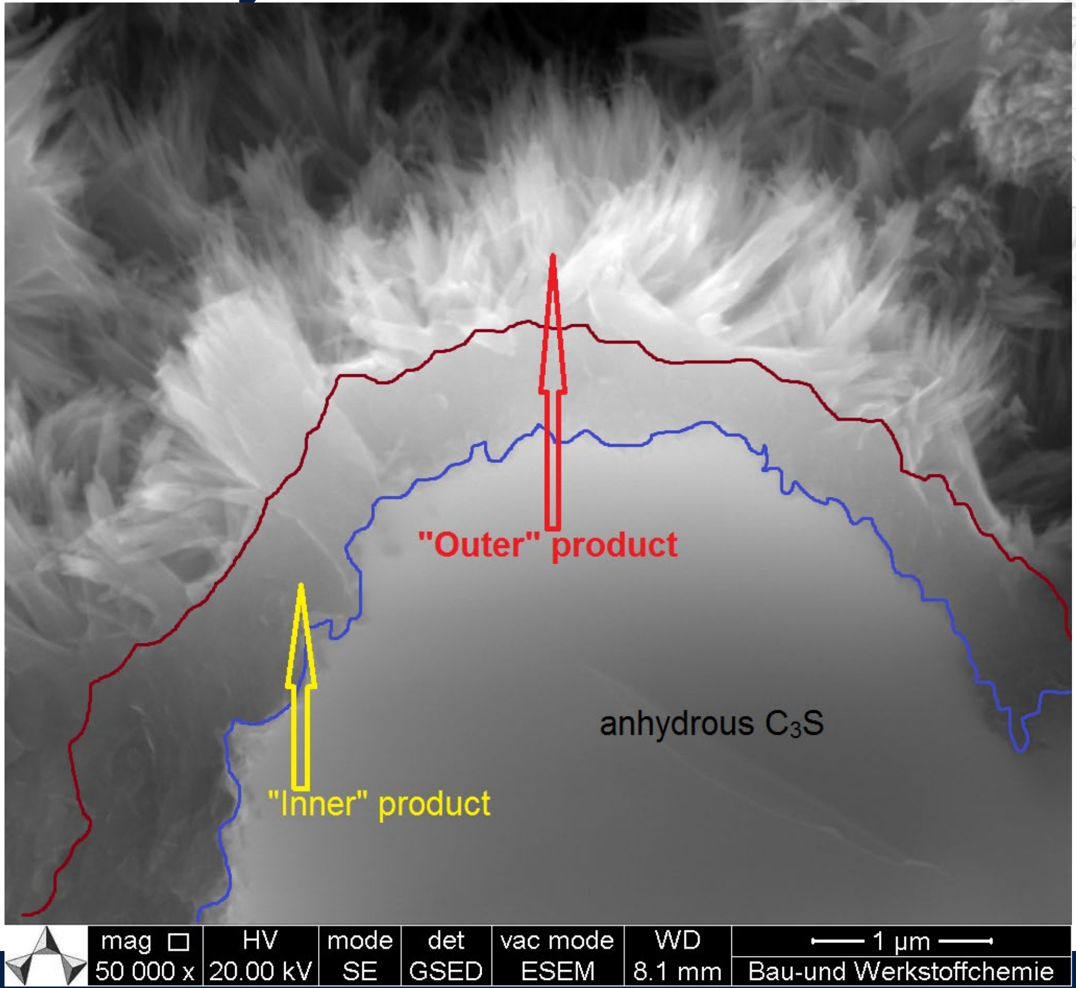


C_3S grain after 96h hydration

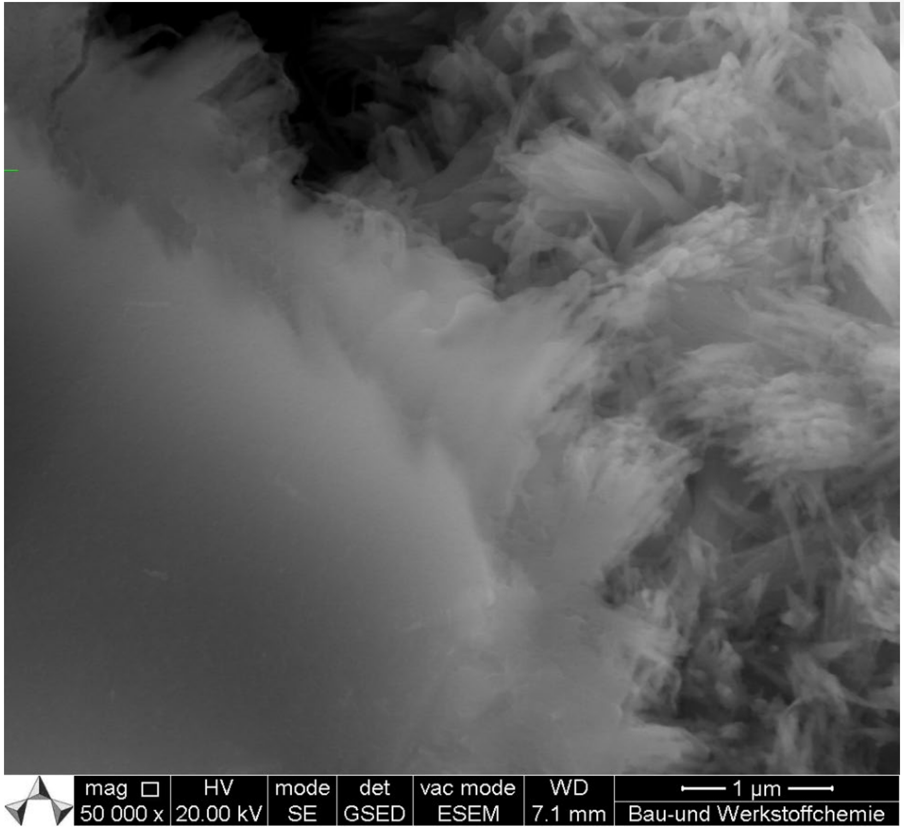




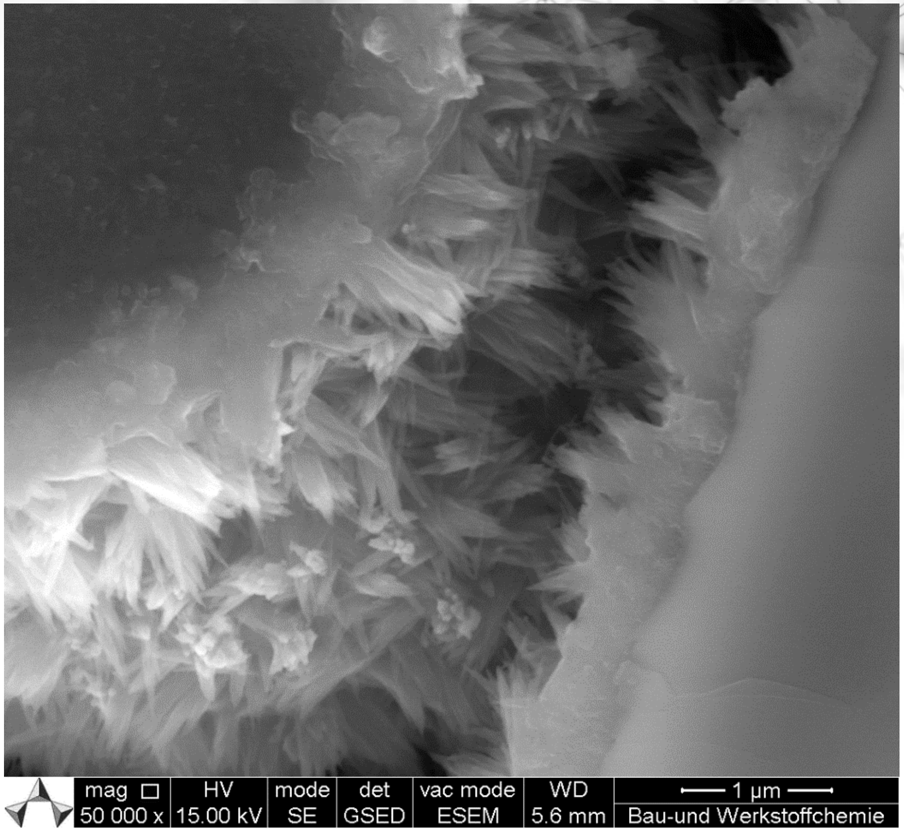
C_3S grain after 96h hydration



C_3S grain after 24h hydration

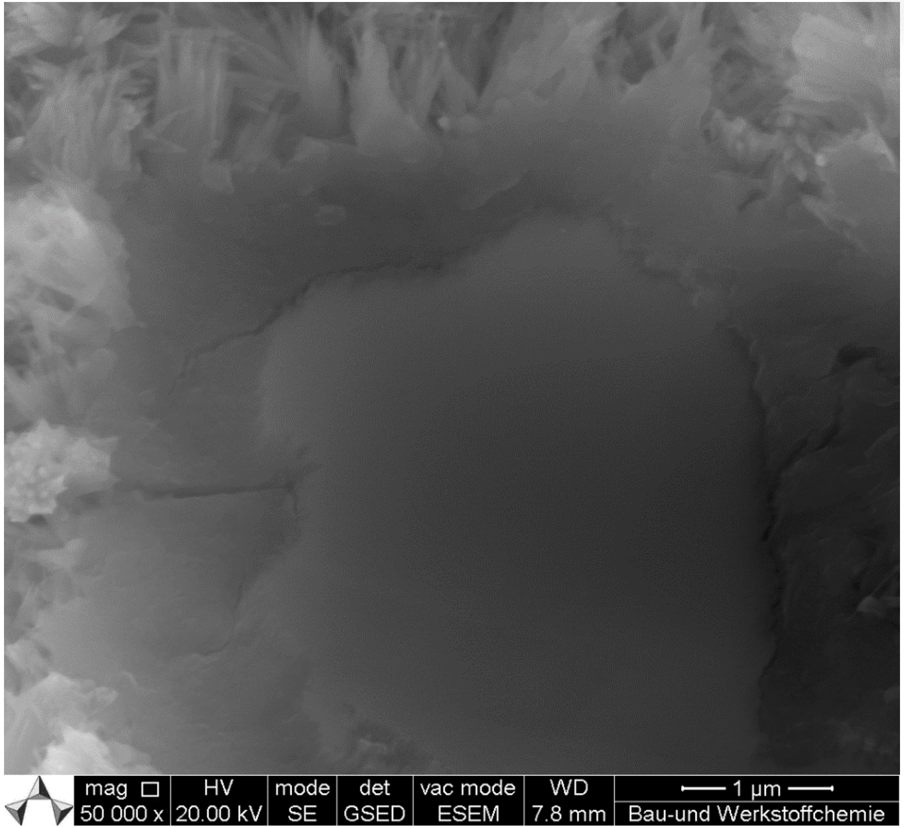


C_3S blank

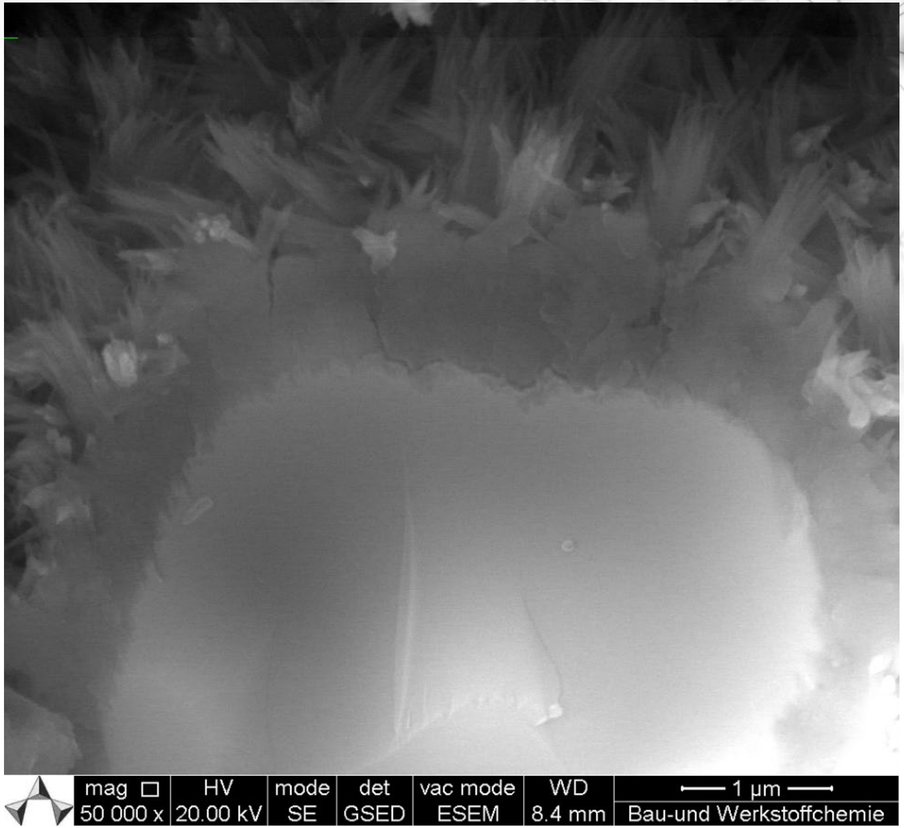


C_3S + nano silicate

C_3S grain after 48h hydration

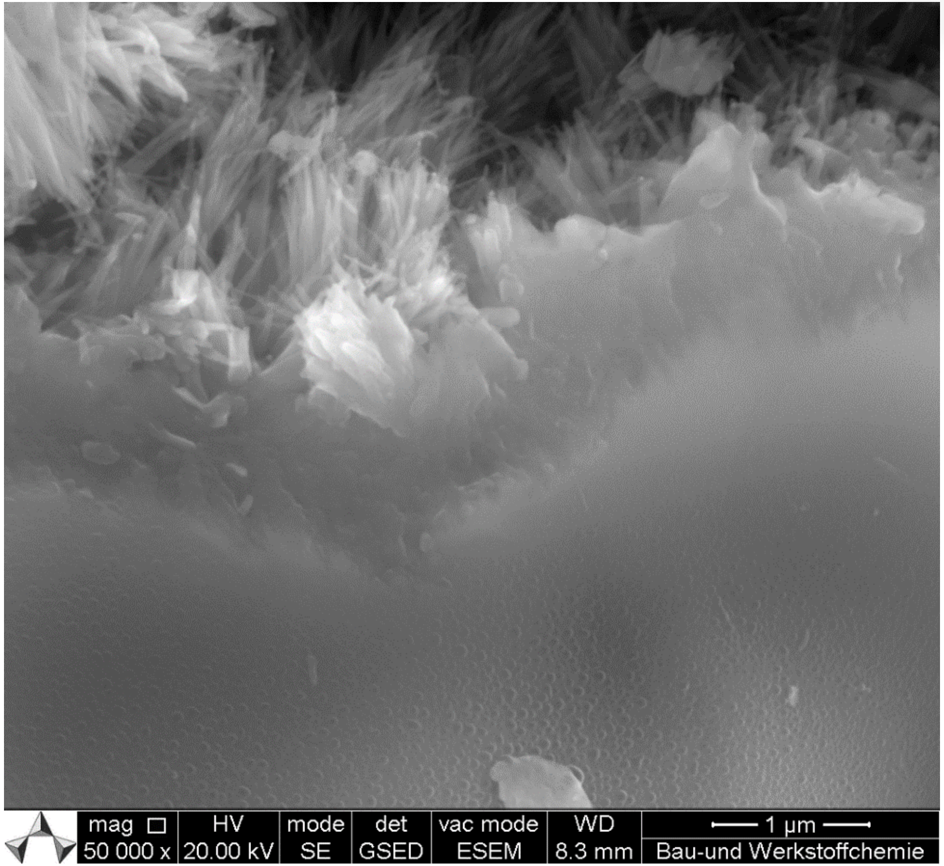


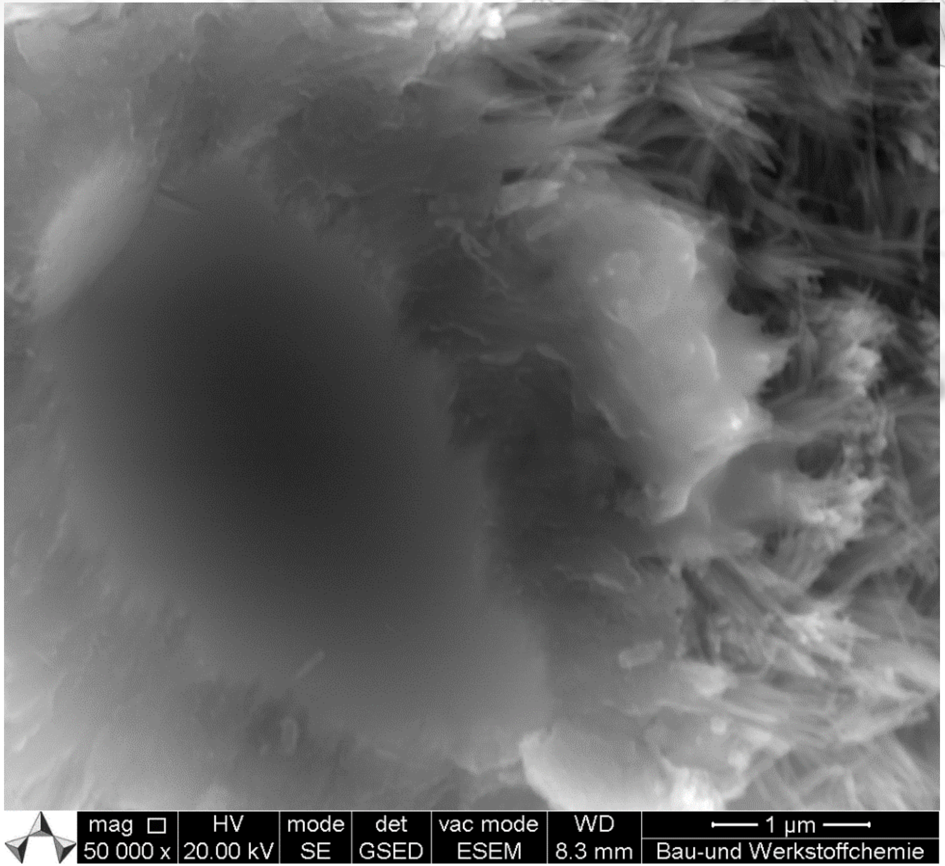
C_3S blank



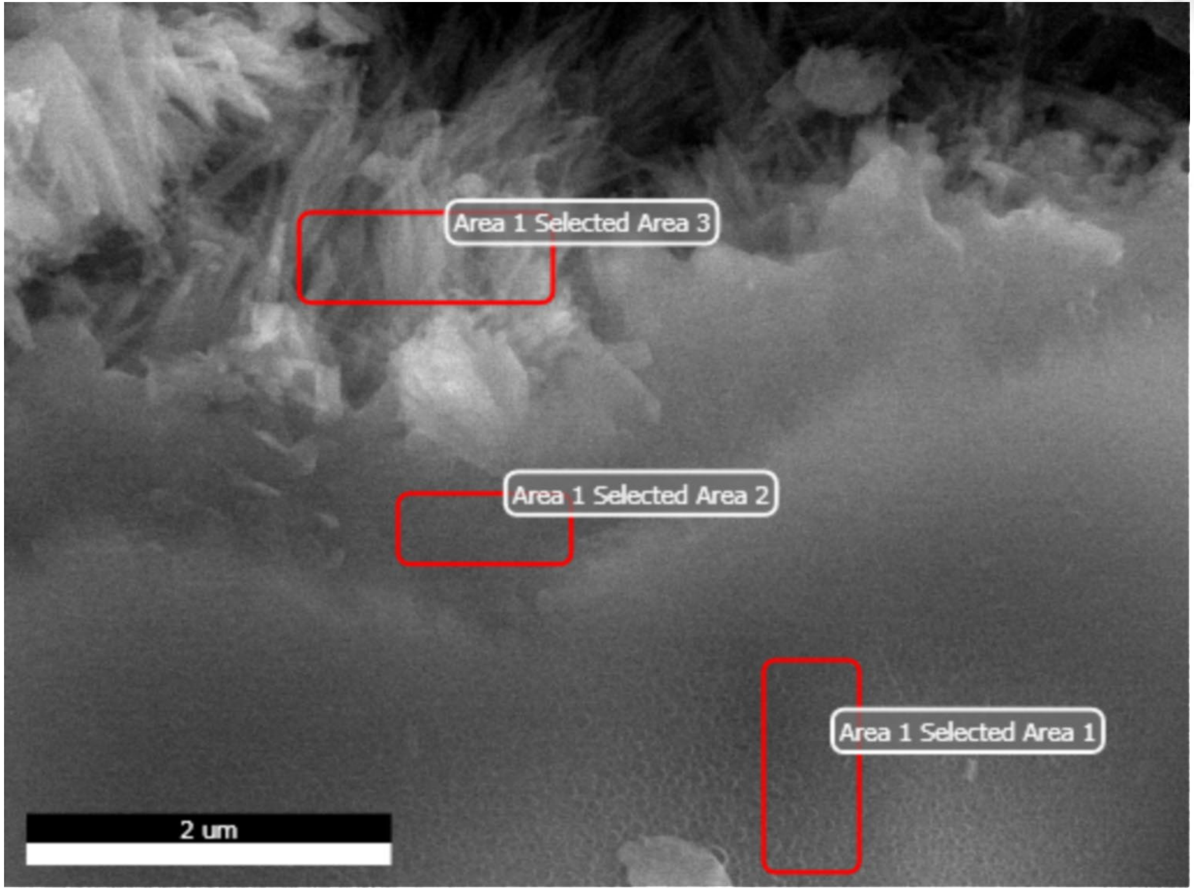
C_3S + nano silicate

C_3S grain after 96h hydration





EDX – Analyses of C_3S after 96 h hydration



	Ca-Weight.%	Si-Weight%	Ca/Si-ratio	O-Weight%
Selected Area 1	55,4	10,5	5,3	34,1
Selected Area 2	50,3	10,0	5,0	39,7
Selected Area 3	53,4	10,4	5,1	36,2

Conclusions

- ✓ These investigations has shown that the formed products of the C_3S hydration using ESEM can very well be characterized

- ✓ ESEM in an aqueous atmosphere without pretreatment and without drying. Therefore different reaction zones and different rehydration products was identified

- ✓ These results show that is to see, there are the differences between unreacted C_3S, “Inner” product and “Outer” product and the different phases are clearly differentiated

Conclusions

- ✓ In conclusion it can be stated that very reliable and new information can be obtained from the results of these investigations, which facilitate the understanding of some processes of the hydration process of C_3S and describe the nano / micro-structure of the formed C-S-H phases.

Vielen Dank an die DFG für die
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