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Transportation Research Record

Xonotlite and Hillebrandite as Model Compounds for C-S-H Seeding in Cementitious Materials

--Manuscript Draft--

Full Title:	Xonotlite and Hillebrandite as Model Compounds for C-S-H Seeding in Cementitious Materials
Abstract:	<p>The demand for more environmentally friendly cement with no disadvantages regarding hydration activity has led to the development of various additives to accelerate cement hydration. Since C-S-H is the major hydration product of cement and is responsible for its mechanical properties, it plays an outstanding role in the discussion of nanoparticle additives. Nevertheless, the investigation of its mechanism of action is complicated by the similarity of its properties to those of the C-S-H that forms as an initial hydration product. Crystalline C-S-H phases, on the other hand, can be easily distinguished from the original hydration products, which makes them a valuable model compound for studying the mechanisms of nucleation seeding in cementitious materials.</p> <p>In this paper, the effect of two crystalline types of C-S-H as nucleation seeds are presented. Xonotlite and hillebrandite were thoroughly characterized by NMR, XRD, SEM, and IR spectroscopy and then used as admixture for alite pastes. Low-vacuum SEM images of the hydrated pastes revealed that xonotlite can significantly promote the visible etch pit formation on C3S clinker particles while this was not found to be true for hillebrandite. Whether the phases act as a nucleation site is assumed to be strongly dependent on the mineralogy: Hillebrandite appeared to be heavily overgrown while xonotlite did not show any hydration products on its surfaces after the same hydration time of up to 24 hours. The diverse effect of the minerals was confirmed by the accelerating behavior in isothermal heat flow calorimetry and by XRD of the hydrated pastes.</p>
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1 **Xonotlite and hillebrandite as model compounds for C-S-H seeding in cementitious materials**

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23

1 **ABSTRACT**

2 The demand for more environmentally friendly cement with no disadvantages regarding hydration
3 activity has led to the development of various additives to accelerate cement hydration.

4 Since C-S-H is the major hydration product of cement and is responsible for its mechanical properties,
5 it plays an outstanding role in the discussion of nanoparticle additives. Nevertheless, the investigation of
6 its mechanism of action is complicated by the similarity of its properties to those of the C-S-H that forms
7 as an initial hydration product. Crystalline C-S-H phases, on the other hand, can be easily distinguished
8 from the original hydration products, which makes them a valuable model compound for studying the
9 mechanisms of nucleation seeding in cementitious materials.

10 In this paper, the effect of two crystalline types of C-S-H as nucleation seeds are presented. Xonotlite
11 and hillebrandite were thoroughly characterized by NMR, XRD, SEM, and IR spectroscopy and then used
12 as admixture for alite pastes. Low-vacuum SEM images of the hydrated pastes revealed that xonotlite can
13 significantly promote the visible etch pit formation on C₃S clinker particles while this was not found to be
14 true for hillebrandite. Whether the phases act as a nucleation site is assumed to be strongly dependent on
15 the mineralogy: Hillebrandite appeared to be heavily overgrown while xonotlite did not show any hydration
16 products on its surfaces after the same hydration time of up to 24 hours. The diverse effect of the minerals
17 was confirmed by the accelerating behavior in isothermal heat flow calorimetry and by XRD of the hydrated
18 pastes.

19

20 **Keywords:** Hillebrandite, Xonotlite, Nucleation Seeding, C-S-H Seeding

1 **INTRODUCTION**

2 Calcium silicate hydrate (C-S-H¹) is the main product of cement hydration and therefore one of the most
3 abundant synthetic materials on earth. The addition of small quantities of C-S-H to cement paste is able to
4 speed up the hydration process significantly at the start of reaction. Compared to conventional accelerators,
5 C-S-H offers various advantages: It neither enhances the corrosiveness nor reduces the long-term strength
6 of the seeded alite, cement, or concrete. Especially in the early hours of hydration, strength gains of up to
7 270% with only 0.3 wt.-% C-S-H seed have been reported, and all studies nevertheless have agreed that the
8 effect was relativized over time [1,2].

9 Although the acceleration of cement hydration through C-S-H is often referred to as “crystal seeding”,
10 direct evidence of the nucleation or growth of hydration products on the synthetic seed has not been reported
11 so far. Indirect methods nevertheless give support to the concept of C-S-H seeding.

12 Nicoleau et al. have investigated the decreasing layer thickness of hydration products on C₃S with and
13 without a commercial seeding agent and concluded that C-S-H growth was transferred to the pore solution
14 through nucleation on the artificial calcium silicate hydrates that were added [3]. Alizadeh et al. have found
15 that the addition of synthetic C-S-H to hydrating C₃S pastes led to the formation of a peak at temperatures
16 above that of the C-S-H seed in differential scanning calorimetry (DSC), which was assigned to the β-
17 wollastonite conversion of hydration products nucleated on the seed. C₃S did not show any peak in the
18 absence of C-S-H seeds [4].

19 The investigation of the changes in hydration product properties induced through C-S-H additions to
20 alite or cement pastes is made complicated by the similarity of both hydrates. Additionally, it is known that
21 the C/S ratio of the naturally formed C-S-H changes while exposed to the pore solution and over time,
22 which is assumed to be valid for the seed too [5]. Hence, the investigation of properties determined by the
23 calcium-to-silicon ratio is difficult to interpret.

24 In contrast to the nano-crystalline C-S-H, the composition of which is commonly only defined by the
25 calcium-to-silicon ratio, more than 40 crystalline calcium silicate hydrate minerals with a defined
26 stoichiometry and properties are known [6–8]. The oldest study regarding their influence on the hydration
27 of cementitious materials that has been published investigated the impact of afwillite (Ca₃(SiO₃OH)₂·2H₂O)
28 on alite pastes. It was found that the afwillite crystals have a decisive influence on the formation of
29 hydration products. Instead of C-S-H I, afwillite was the main hydration product, which was attributed to
30 the low differences in the free energy of afwillite to tobermorite such as C-S-H [9]. The results have recently
31 been confirmed by Horgnies et al., who investigated the impact of afwillite on numerous properties of
32 hardened pastes and found beneficial as well as problematic changes [10]. The addition of gyrolite

¹ Cement chemistry nomenclature: C = CaO, S = SiO₂, H = H₂O

1 (Ca₁₆Si₂₄O₆₀ (OH)₈·14(H₂O)) has been investigated by Eisinas et al. in great detail. The additive was found
2 to interact in a complex manner with the pore solution. It was proposed that the C₃S dissolution was
3 accelerated through the adsorption of calcium ions, which finally resulted in the recrystallization of gyrolite
4 to C-S-H I. In addition, hydration products were assumed to have grown on gyrolite crystals [11]. In 2015
5 Land et al. investigated xonotlite (Ca₆[Si₆O₁₇](OH)₂) and a mineral of the tobermorite group (unknown
6 phase) and found that only extraordinarily high concentrations induced a significant impact on the heat flow
7 [12].

8 The aim of the current study was to investigate the effect of crystalline C-S-H phases as model
9 compounds for seeding applications in general. Therefore, 2 different phases with comparable properties
10 were chosen: hillebrandite (Ca₂SiO₃(OH)₂), whose structure is made of 3-periodic single silicate chains,
11 and xonotlite, which contains 3-periodic double silicate chains. These represent thermodynamic end
12 members of their respective calcium-to-silicon ratio. The comparatively easy preparation without side
13 products, high- as well as low-calcium content, and the fiber-like morphology make them suitable for
14 subjected investigation. Additionally, recrystallization of the seed or induced product formation in the
15 cementitious system were regarded as unlikely, since both are thermodynamically stable, high-temperature
16 phases whose free energy difference to C-S-H is assumed to be high. [13,14].

17 18 **METHODS**

19 Xonotlite and hillebrandite were synthesized hydrothermally from nano-crystalline C-S-H prepared in
20 advance. For the synthesis of the nano-crystalline C-S-H, the starting materials calcium oxide (calcined at
21 950 °C, VWR), silicon dioxide (Köstrosol 0730, CWK), and demineralized water were mixed in the desired
22 calcium-to-silicon (Ca/Si = 1 or 2) and water-to-solid ratio (w/s = 10). The suspension was transferred to
23 plastic bottles and kept under constant agitation in a shaker for 24 hours, which allowed complete reaction
24 as was demonstrated in [15]. Hydrothermal reactions were carried out in stainless steel autoclaves with
25 Teflon inlays at 200 °C for 3 days. The samples were freeze dried for analysis and application.

26 The mineralogy of the samples was investigated by X-ray diffraction (PANalytical Empyrian, PIXcel
27 1D Detector, Cu K α , *Panalytical*), magic angle spinning nuclear magnetic resonance spectroscopy of the
28 ²⁹Si core (Avance 400, 400 MHz, *Bruker*), infrared spectroscopy with a diamond crystal for attenuated total
29 reflection (Spectrum Two with UATR Two, 32 scans, 4000-400 cm⁻¹, *PerkinElmer*), and scanning electron
30 microscopy (GeminiSEM500 NanoVP, low vacuum, *ZEISS*). For SEM images, the samples were attached
31 to carbon pads with minimal force to avoid drastic structural changes in the clinker. No metal sputtering
32 was necessary.

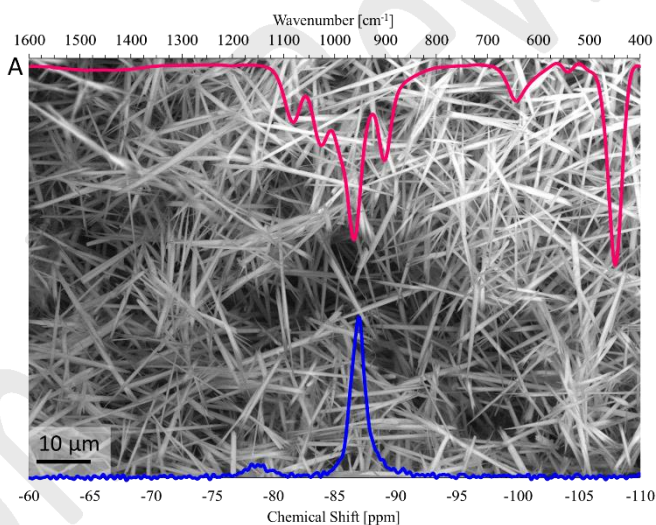
33 Triclinic C₃S was prepared by the VUSTAH Research Institute for Building Materials in Brno, Czech
34 Republic.

1 Information about the impact on the heat of hydration were obtained by calorimetry of 5g cement (CEM
2 I, 52.5 R, CEMEX) or 2g C₃S externally mixed with water in a ratio of 0.5. The additives were dispersed in
3 the water by ultrasonification, the same as for SEM samples. All measurements were repeated 3 times.
4 (Isothermal heat flow calorimeter MC-CAL100, 20 °C, C3 Analysentechnik).

5 C₃S was mixed with 5wt.-%, in water-dispersed crystalline C-S-H to obtain the pastes for SEM
6 investigations. The water-to-binder ratio was raised to 1.1 to obtain a mixable paste of standard consistency.
7 The samples were stopped after 2 and 24 hours by solvent exchange with isopropanol and dried at 40 °C.

9 RESULTS

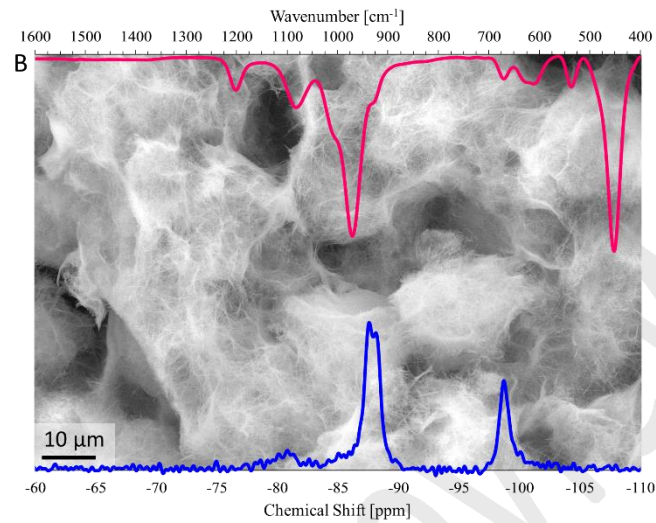
10 The synthesis yielded white powders that were characterized by XRD, ²⁹Si-NMR, IR, and SEM. The
11 sample prepared with Ca/Si = 2 formed needles with frayed tips, with an average size of 10x1 μm, that
12 were loosely stacked but not agglomerated. All X-ray reflexes could be assigned to ICSD 98-008-0127, and
13 the NMR spectrum showed peaks matching Q¹ and Q² silicate units as expected for hillebrandite (Figure 1
14 SEM image and NMR spectrum in blue, data in table 1).



15
16 **Figure 1: The sample prepared at 200 °C with a Ca/Si of 2 was found to consist of large needles (SEM**
17 **image). The IR (pink, top) and ²⁹Si-NMR spectra (blue, bottom) confirmed that hillebrandite was**
18 **formed.**

19
20 The mean chain length (\overline{CL}) of hillebrandite was calculated according to $\overline{CL} = (2(Q^1 + Q^2))/Q^1$ to
21 be 22. The infrared spectrum showed vibrational and rotational frequencies assigned to Q¹ and Q² silicates
22 in the range of 400 to 1200 cm⁻¹, confirming the presence of Q¹ and Q² species as found in ²⁹Si-NMR spectra
23 (Figure 1 pink line, data in table 1).

1 Xonotlite was prepared with a initial Ca/Si ratio of 1.0, it formed long fibers with 0.1 μm average
2 thicknes that were interwoven and connected to spider-web like structures (Figure 2). The morphology was
3 found to be significantly finer compared to hillebrnadite.
4



5
6 **Figure 2: The sample prepared at 200 °C with a Ca/Si of 1 was composed of fine, web-like fibers**
7 **(SEM image). The IR (pink, top) and ^{29}Si -NMR spectra (blue, bottom) confirmed that xonotlite was**
8 **formed (Compare table 1).**

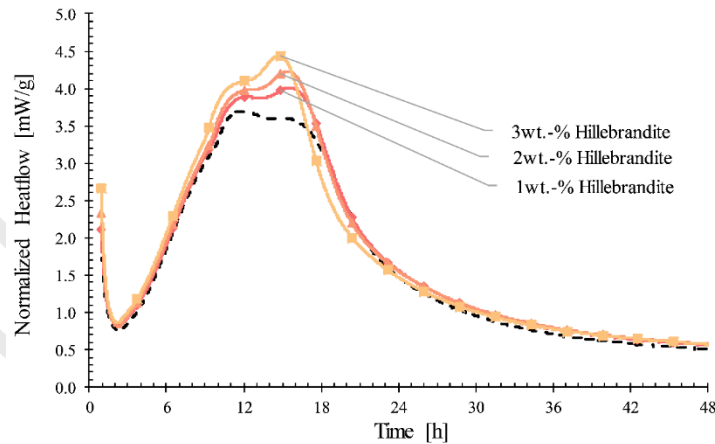
9
10 Xonotlite contains double chain silicates, hence, in contrast to hillebrandite, Q^3 signals were found at
11 1200 cm^{-1} in IR and -98.8 ppm in ^{29}Si -NMR spectra. Additionally, the Q^2 peak in NMR is split due to the
12 two different silica positions with different binding angles in xonotlite (Figure 2). Based on an ideal
13 xonotlite crystal, the ratio of Q^2/Q^3 would be 2 with no Q^1 at all. The actual distribution of silicate species
14 with a $\text{Q}^2/\text{Q}^3 = 1.54$ and 16% Q^1 silicates indicates a heavily disturbed crystal structure. The reflexes in
15 XRD could be assigned best to the Ma2b2c polytype of xonotlite described by ICSD 98-009-4484; no
16 reflexes of foreign minerals were found. Table 1 summarizes the peak positions of infrared and NMR
17 analysis of both minerals.
18

19 **Table 1: Peak positions and calculated silicate polymerization from ^{29}Si -NMR and positions of IR**
20 **bands of samples shown in figures 1 and 2.**

	Q ¹	Q ²	Q ³	$\tilde{\nu}$ (cm ⁻¹)
Xonotlite	-80.7 ppm 16 %	-87.6 ppm 40 % (Si1) -88.3 ppm 19 % (Si2)	-98.8 ppm 26 %	1202, 1082, 1008, 971, 928, 670, 630, 610, 536, 452
Hillebrandite	-78.6 ppm 9 %	-87.0 ppm 91 %	-	1081, 1025, 961, 902, 642, 541, 506, 448

1
2 For application as an additive to cement or alite pastes, the dried calcium silicate hydrates were dispersed
3 in water with an ultrasonic rod. Especially xonotlite made handling complicated since it is very voluminous.
4 Calorimetry concentrations up to 3wt. % of xonotlite in cement were workable at w/c = 0.5 but increased
5 the viscosity strongly.

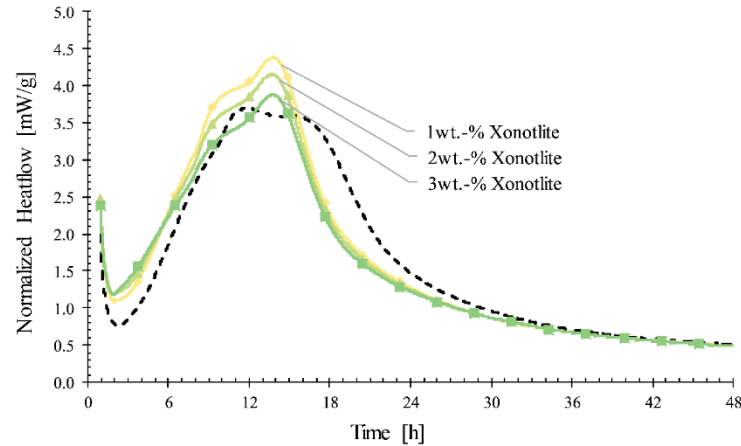
6 Cement seeded with hillebrandite did not show any change up to 8 hours of hydration, after which the
7 effect became visible in an enhanced maximum heat flow. Higher dosages of hillebrandite increased this
8 effect (Figure 3). Additionally, it was visible that the sulfate depletion became the main peak and was also
9 greatly enhanced by higher concentrations of the additive. Nevertheless, no shift in the hydration periods
10 over time was recorded, which means that hillebrandite did not accelerate the hydration.



11
12 **Figure 3: The addition of 1-3 wt.-% hillebrandite to cement resulted in a higher maximum heat flow**
13 **but no acceleration of the hydration periods. Higher dosages of hillebrandite enhanced the effect on**
14 **the peak maximum.**

15
16 Surprisingly, the addition of xonotlite to cement shows a different effect compared to that of
17 hillebrandite in many details. The heat flow during the dormant period was visibly enhanced, and the

1 acceleration period started earlier compared to the reference cement. Higher dosages of xonotlite appeared
2 to be less beneficial after the dormant period, but as it was also found for hillebrandite, the sulfate depletion
3 was affected more by the additive than the silicate reaction peak and became the main maximum (Figure
4 4).

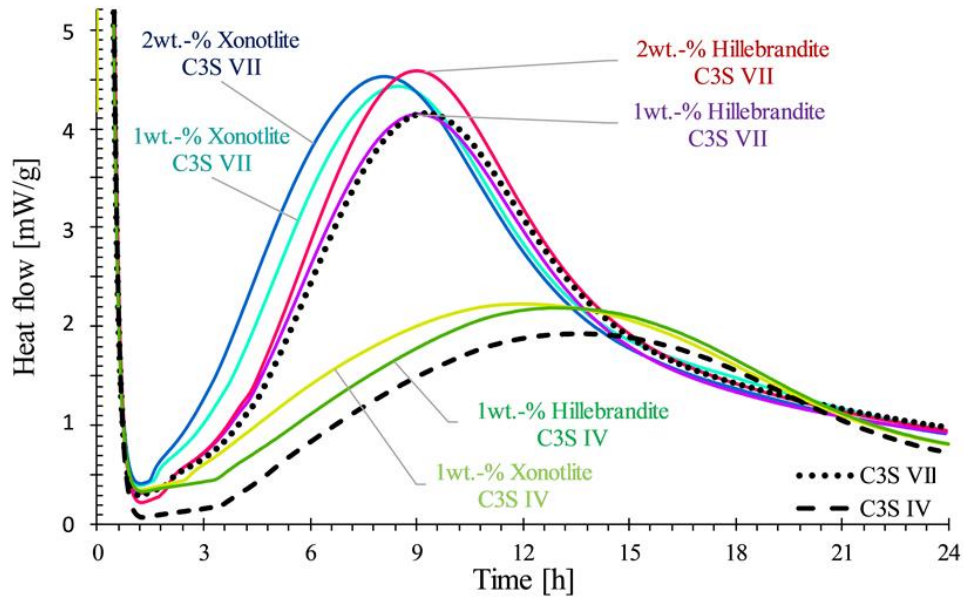


5
6 **Figure 4: The addition of 1-3 wt.-% xonotlite to cement resulted in an enhanced heat flow during the**
7 **dormant period, a higher maximum, and a slight acceleration of the hydration periods. Higher**
8 **dosages of xonotlite reduced the effect on the peak maximum.**

9
10 Although both additives showed a positive impact on hydration, their effect was found to differ in
11 various points. Therefore, it was concluded that the fundamental mechanism might also be different.
12 Amorphous C-S-H is known to accelerate cement mainly through its impact on the silicate reaction. For
13 this reason and because the heat release during the first 12 hours is almost completely attributed to the
14 silicate reaction [16], it was decided to investigate the impact of hillebrandite and xonotlite on a pure silicate
15 system.

16 The calorimetry investigations in pure C_3S were conducted with two batches of clinker ground to
17 different finesses: C_3S IV with a lower fineness and C_3S VII with a higher fineness. The additive
18 concentration was varied only for C_3S VII. The experiments were done with low amounts of C_3S paste (2g),
19 and a baseline correction was necessary to account for the heat flow during the dormant period that was
20 below zero for the coarse batch. The results were nevertheless congruent to the results obtained in cement:
21 Hillebrandite enhanced the maximum heat flow but did not accelerate the reaction; xonotlite did accelerate
22 the hydration moderately but enhanced the heat flow less than hillebrandite. A difference was found
23 regarding the impact of the xonotlite concentration: in cement, a higher concentration led to a decreased
24 benefit, but in C_3S the higher dosage led to a more pronounced acceleration. This deviation was expected,
25 since many additives have an optimal concentration determined by the clinker specification. Another
26 deviation found in the coarser clinker batch (C_3S IV) was that hillebrandite apparently enhanced the heat

1 flow during the dormant period. However, since the experiments were conducted with a low amount of
2 paste, the heat flow rates close to zero are prone to baseline errors, and this effect of hillebrandite therefore
3 needs further investigation.



4
5 **Figure 5: The addition of 1 and 2 wt.-% xonotlite or hillebrandite to C₃S ground to a different**
6 **fineness. The dashed lines indicate C₃S IV with a lower fineness and the solid line indicates C₃S VII.**

8 To investigate whether one or both mineral phases act as a template for hydration products to grow or
9 alter the nucleation of C-S-H in another way, triclinic C₃S was hydrated with or without additives and
10 stopped after short time intervals. The short hydration time was chosen to see the clinker grains at a stage
11 where they should not be overgrown by hydration products too much.

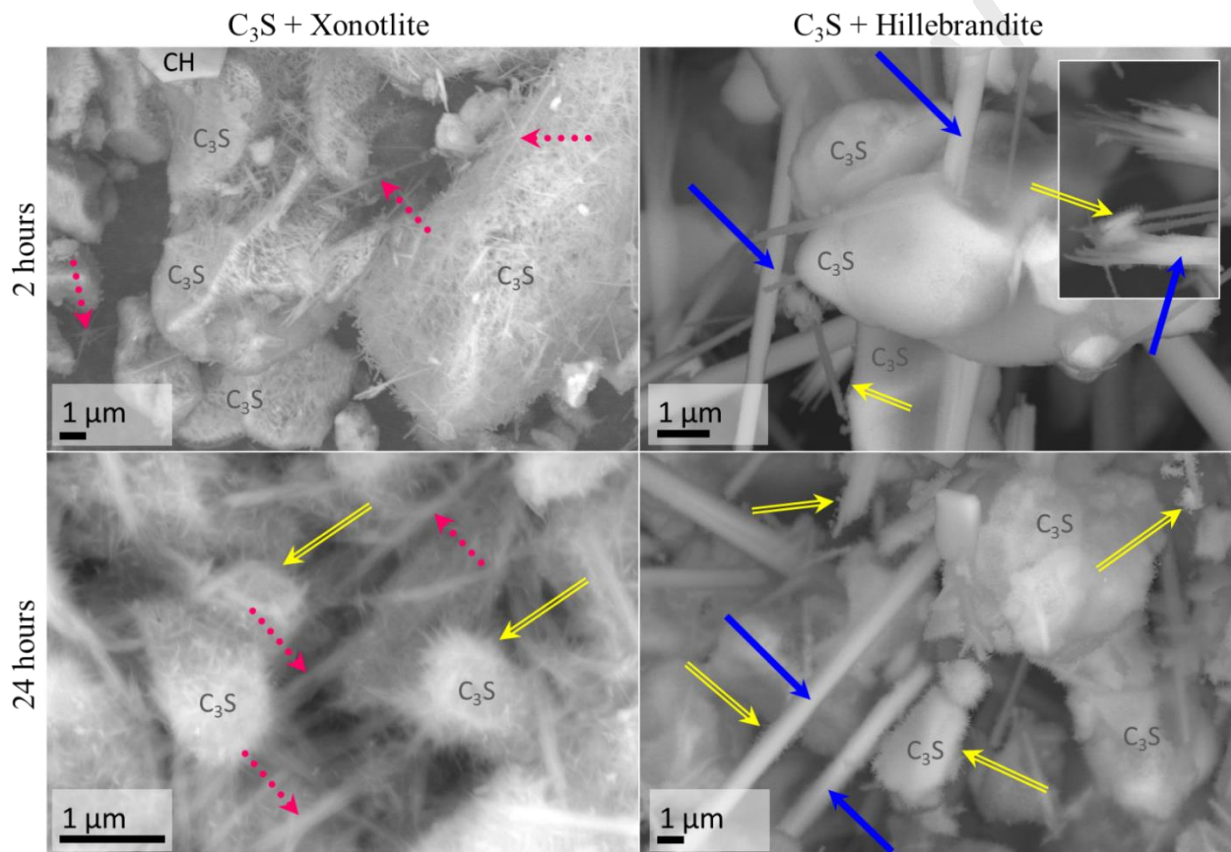
12 For the preparation of the SEM samples, the water-to-C₃S ratio had to be elevated to 1.1 to allow the
13 preparation of a mixable paste with 5wt.-% calcium silicate hydrate. The concentration of the additive was
14 enhanced for the practical consideration of finding the fibers under the microscope. Samples were stopped
15 after 2 and 24 hours and examined after drying through solvent exchange with isopropanol. Figure 6 shows
16 the SEM micrographs of C₃S seeded with xonotlite or hillebrandite after 2 and 24 hours. Both xonotlite
17 (dotted pink arrows in figure 6, 2 hours) and hillebrandite fibers (solid blue arrows) were evenly distributed
18 throughout the clinker grains.

19 C₃S mixed with xonotlite showed a prominent formation of etch pits after two hours, while in the paste
20 with hillebrandite, no etch pits were detectable on the clinker surface at that time of hydration. Portlandite
21 crystals were found in the 2-hour xonotlite sample but no hints of C-S-H formation. This might indicate the
22 finely distributed growth of C-S-H. In the 2-hour hillebrandite sample fine fibers nevertheless formed at

1 the frayed edges of hillebrandite needles and on clinker surfaces that are assumed to be C-S-H (inset in
2 figure 6, double lined yellow arrows indicate hydration products).

3 After 24 hours of hydration, C-S-H was found nucleated on clinker grains in both samples (double-lined
4 yellow arrows). Nevertheless, xonotlite fibers did not seem to be overgrown with hydration products, while
5 hydration products formed needles on all hillebrandite. The hydration product needles formed in the
6 xonotlite-seeded sample appeared to be of a similar dimension as in the hillebrandite-seeded sample. The
7 experiment was repeated with a C₃S batch of a different Blaine fineness with matching results.

8



9

10 **Figure 6: C₃S with the addition of 5 wt.-% xonotlite or hillebrandite after 2 and 24 hours of hydration.**
11 **Clinker particles (C₃S) and Calcium hydroxide (CH) are labelled. Xonotlite needles (pink, dotted),**
12 **hillebrandite needles (blue, solid), and C-S-H (yellow, double lined) are indicated with arrows.**

13

14 The crystalline phases of the hydrated pastes investigated by scanning electron microscopy were
15 analyzed by XRD to confirm the observations. The calcium hydroxide content of xonotlite-seeded samples
16 was approximately 5 times higher than in the hillebrandite-seeded sample after 2 hours, which complements
17 the findings from SEM and calorimetry. After 24 hours, the xonotlite sample still contained more calcium
18 hydroxide than the hillebrandite sample, but the difference was reduced.

1 An induced product formation as reported by Seligmann et al. and Horgnies et al. for afwillite was not
2 found for the two investigated phases. The fiber formation on hillebrandite needles was therefore attributed
3 to C-S-H.

5 **DISCUSSION**

6 Overall, the aforementioned results draw a conclusive picture of two different types of hydration
7 modifiers. In the following, the dormant and acceleration period will be discussed in detail.

8 The main difference of the two samples investigated after 2 hours was the strong manifestation of etch
9 pits on clinker grains in the xonotlite-seeded sample. As Nicoleau stated in 2016, this does not necessarily
10 mean that no or fewer etch pits are formed in the hillebrandite sample, but that they are more visible in
11 xonotlite-seeded samples due to a lack of overgrowth [17]. Nevertheless, x-ray analysis of the samples
12 confirmed that more portlandite was formed in the xonotlite-seeded sample, which confirms an accelerated
13 dissolution of tricalcium silicate.

14 The enhanced dissolution of tricalcium silicate is determined by a higher degree of undersaturation with
15 respect to C_3S [18,19]. A higher undersaturation in a pure system can only be achieved through a faster
16 nucleation of C-S-H, which is believed to be the rate-determining step [19]. No amorphous calcium silicate
17 hydrate that could be accountable for the increased undersaturation was identifiable in the xonotlite-seeded
18 sample, which could mean that the hydration product was very finely distributed over clinker particles and
19 the large area of the xonotlite fibers. The xonotlite fibers, however, were not visibly overgrown even after
20 24 hours, except when they were lying directly on top of clinker grains. Another explanation could be a
21 concentration gradient induced by xonotlite without a detour over C-S-H. Xonotlite is known to exchange
22 its calcium rapidly for various bivalent ions such as magnesium, cobalt, and nickel, which indicates that the
23 calcium ions in xonotlite are rather mobile. Ongoing experiments are investigating whether xonotlite can
24 uptake or release calcium ions from its structure and hence vary its C/S ratio to a small degree [20,21].
25 Since xonotlite wires were found to be coiled around clinker grains, this might favor local concentration
26 gradients in the direct vicinity to the additive.

27 In consideration of the results of Seligman et al. and Horgnies et al. [9,10], induced product formation
28 might also explain the lack of hydration products in combination with an accelerated dissolution. This was
29 nevertheless found unlikely since xonotlite is a high-temperature phase, and x-ray analysis did not show
30 any increase of xonotlite or hillebrandite in the samples that could account for any relevant effect. For the
31 same reasons, this is valid for the recrystallization theory reported by Eisinias et al. in the case of gyrolite
32 [11].

33 Although it cannot be clarified yet which of the three theories is valid, the fact that a higher xonotlite
34 concentration slightly enhances its effect on the dormant period does not contradict any of them.

1 Hillebrandite did not alter the dormant period and hence did not drastically change the nucleation kinetics
2 of C-S-H during that time, although some hydration product grew on the needles.

3 Both samples were prepared with a w/c of 0.5, and the viscosity of the pastes increased drastically. Both
4 mineral additives are expected to have a strong impact on the water mobility due to their high surface area.
5 This can explain the effect of higher heat flow with higher hillebrandite concentrations, since a similar
6 effect occurs in pastes with a lower water content [22]. To a lesser extent, this is probably also valid for
7 xonotlite, but the reduced heat flow with a higher dosage cannot be explained by the reduced water-to-
8 binder ratio. Experiments in conditions with excess water might be able to clarify the effects.

9 The peak of the acceleration period is assumed to be strongly correlated to the growth of hydration
10 products, although the detailed mechanism is still under debate [23]. Consequently, after 24 hours, the most
11 dominant optical difference between the two samples were the hydration products. The relatively large
12 hillebrandite needles were covered with perpendicularly growing C-S-H fibers, while the xonotlite fibers
13 did not show such a prominent overgrowth with C-S-H. This indicates that hillebrandite provides a better
14 template for the nucleation of hydration products. The crystal structure of hillebrandite is made of a three-
15 dimensional network of calcium polyhedrons. In water, a part of the surface-oriented calcium is assumed
16 to be released due to the lower concentration of calcium in the pore solution. The locally high calcium
17 concentration around hillebrandite might allow an easier nucleation of C-S-H through local oversaturation
18 as found for limestone [22].

19 The most interesting question that results from the presented research is what causes the different effects
20 of the two additives. A detailed investigation of the pore solution of hydrating pastes is needed to clarify
21 the impact of xonotlite and hillebrandite. Furthermore, possible structural changes in the minerals exposed
22 to synthetic pore solution or water will be investigated to clarify if ion uptake or release can induce the
23 described effects. Although the morphology of hillebrandite and xonotlite was always found to be fiber- or
24 needle-like, changes can be induced with the hydrothermal treatment time. It was possible to prepare
25 xonotlite fibers of a similar morphology as hillebrandite and hillebrandite needles of different dimensions.
26 Additionally, the size of the structures can be broken down through milling processes. Ongoing work is
27 focusing on the impact of different particle sizes and morphologies as well as different silicate
28 polymerizations of the same minerals. Besides xonotlite and hillebrandite, it has been possible to synthesize
29 other crystalline C-S-H phases as well, and their impact on product nucleation and C_3S dissolution is
30 currently under investigation. The systematic investigation of different crystalline phases and modifications
31 of hillebrandite and xonotlite will bring more insight into the effects that are caused, and in a final step
32 these findings will be transferred to nano-crystalline C-S-H.

33

34 **SUMMARY & CONCLUSION**

1 The two crystalline calcium silicate hydrates xonotlite and hillebrandite were prepared by a simple
2 hydrothermal approach. Thorough analysis of their properties revealed no byproducts and confirmed their
3 typical properties, such as silicate polymerization and morphology.

4 The addition of xonotlite or hillebrandite to cement or alite pastes moderately accelerated the hydration.
5 The minerals have been found to exert a remarkably different impact on the hydration kinetics despite their
6 similarities. Xonotlite enhanced the heat flow during the dormant period and shifted the hydration periods
7 to an earlier time in calorimetry. Its positive effect was reduced with higher concentrations. SEM images
8 revealed that it had enhanced the C₃S dissolution, which was confirmed by XRD. Hillebrandite, on the other
9 hand, has not altered the dormant period of seeded cements but has enhanced the maximum heat flow
10 without shifting the hydration periods in time. Higher concentrations enhanced its effect. Both phases were
11 not found to induce the formation of hydration products other than calcium hydroxide or C-S-H I, and both
12 phases had a stronger impact on the heat development due to sulfate depletion than on heat development
13 due to the silicate reaction.

14 It is assumed that the reason for the deviations originates from the mineralogy of the C-S-H and might
15 provide interesting insights into nucleation seeding in the future.

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22 **AUTHOR CONTRIBUTIONS**

23 The authors confirm contribution to the paper as follows: study conception and design: E. John; data
24 collection: C. Lehmann, E. John; analysis and interpretation of results: E. John; draft manuscript
25 preparation: E. John. All authors reviewed and discussed the results and approved the final version of the
26 manuscript.

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