

Structure of Supercritically Dried Calcium Silicate Hydrates (C-S-H) and structural
Changes Induced by Weathering

Victor Morales-Florez^{a,b*}, Nicolas de la Rosa-Fox^c

a- Instituto de Ciencia de Materiales de Sevilla (ICMS, CSIC-Universidad de Sevilla). Av. Américo Vespucio 49, 41092, Sevilla (Spain)

b- Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Sevilla. Av. Reina Mercedes s/n, Sevilla, 41012 (Spain)

c- Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cádiz. Av. Republica Saharaui s/n 11510 Puerto Real, Cadiz (Spain)

Abstract

The nanostructure of supercritically dried calcium silicate hydrates was researched. This particular drying procedure was used to avoid nanostructure modifications due to conventional drying processes. Thus, in this work, the as-precipitated cementitious C-S-H structure was obtained for the first time. A specific surface area 20% larger than conventionally dried C-S-H was measured. Given the importance of this nanostructured phase for the properties of hydrated cements, especially when in contact with CO₂-rich environments, the supercritically dried C-S-H was weathered for two weeks. The structural effects of this weathering process on the C-S-H were researched and calcium carbonate microcrystal precipitation or the presence of silica by-product are reported. Calcite and aragonite polymorphs were observed, as well as nanoporous silica forming globular arrangements. In addition, two weeks of weathering was not enough to carbonate the entire C-S-H sample.

Introduction

Despite cementitious construction materials are known and used for millennia, the nanostructure of their main binding phase, calcium silicate hydrate (C-S-H)^{*} [1] is not completely understood yet. C-S-H is a porous particulate quasi-mineral of variable composition which is formed by the hydration of the C₂S and C₃S phases of the cement. It plays a central role in the properties of hydrated cements, such as mechanical properties or durability of the cementitious buildings. Moreover, the reactivity of hydrated cements with carbon dioxide, such as atmospheric (weathering effect) or from carbon capture geological storage, also depends on this calcium-rich phase [2, 3]. Consequently, it is crucial to evaluate the properties of hydrated cements when exposed to CO₂ [4-6] and specially to understand the structural changes due to carbonation.

There is some controversy on the structure of this porous phase given the heterogeneity in particle shape and in the chemical composition of the C-S-H phase. The scientific community has assumed the coexistence of two types of C-S-H depending on where they precipitate with respect to the parent anhydrous C_xS grains, namely, in the pore space among the original clinker grains or in the space initially occupied by them. This binary description has been described as low density C-S-H (LD) and high density (HD), respectively [1, 7-9][†]. LD C-S-H is a broad, low dense phase with sheet-like and needle-like particle morphologies, whereas HD C-S-H is a

* Cement notation: C:CaO; S:SiO₂; H:H₂O. The hyphenation shows variable composition.

† In cement science, there are several classifications for the different types of C-S-H, namely, outer product (OP) and inner product (IP), C-S-H Type I and Type II, etc. In this work, we do fall into a discussion on these classifications, but remark on the complexity of the nanostructure.

1
2 rough and denser disordered particulate matrix. Transmission electron microscopy
3 (TEM) imaging clearly illustrates the aforementioned types of C-S-H [10].

4
5 These nanostructures can be described as assemblages of random packings of
6
7 nanocrystalline particles several nanometres in size, arranged in several hierarchical
8
9 levels, where embedded water molecules can be found [9-13]. This phase eventually
10
11 extends through the space between resting non-reacted mineral grains [14]. Small
12
13 angle scattering experiments (SAXS if x-rays are used as radiation, or SANS if neutrons
14
15 are used) have been performed to research C-S-H structure during hydration of the
16
17 cement [15], reporting the surface fractal morphology of C-S-H [16] eleven hours after
18
19 the hydration of cement on a length scale of 10-100 nm. These experiments also
20
21 revealed some characteristic features such as the multi-level nature of the structures,
22
23 the density and the role of water in the basic building blocks [17, 18]. In fact, size,
24
25 shape, crystallographic nature, water content and their arrangements forming
26
27 hierarchical fractal structures, have been the focus of several research works, both
28
29 experimentally [19-21] and computationally [13,22]. Tobermorite or jennite are being
30
31 proposed as their crystallographic and chemical nature [10, 23].
32
33
34
35
36
37
38

39 Regarding the reactivity with CO₂, studies on the structural changes of cementitious
40
41 calcium-rich phases due to carbonation have previously shown that ~50 nm clusters
42
43 and pores with radii between 2 nm and 7 nm appear under the influence of different
44
45 environments containing CO₂ [24], mainly due to the carbonation of the low-density C-
46
47 S-H [25]. Fast carbonation due to atmospheric CO₂ has been reported [26], especially
48
49 for calcium-to-silica ratio over 0.75 [27]. However, no significant change in the specific
50
51 surface area has been observed [28].
52
53
54

55 In this work, a new technique for obtaining and studying cementitious C-S-H was
56
57 used, and a new perspective on the structural research of this important binding
58
59
60
61
62
63
64
65

nanoporous material is proposed. It has been stated for almost a century that the drying process of nanoporous structures leads to the collapse of the structure itself, given the huge interpore forces that appear due to the surface tension of the liquid-gas interface that are inversely proportional to pore radius. To avoid these huge tensions, the liquid-gas interphase should be avoided when removing the solvent. This is achieved by raising temperature and pressure over the critical point of the solvent (243 °C and 63 bar for ethanol) and then removing it under supercritical conditions [29]. Typically, hydrated cement samples and synthetic C-S-H are necessarily dried to perform research based on several characterisation techniques (TEM, SEM, nitrogen physisorption, typical SAXS or SANS experiments). Consequently, the C-S-H structure that has been studied is not the same as was precipitated in the original aqueous phase, prior to drying. In this work, we have used the supercritical drying process to obtain and study the C-S-H structure, not dramatically affected by the conventional drying process. To our knowledge, this is the first time that the study of the original as-precipitated nanostructure of C-S-H has been performed under dry conditions.

Materials and methods

Synthesis and weathering

The C-S-H sample was synthesised from a solution with a Ca/Si molar ratio of 1.8 according to the co-precipitation method [30] which consists of adding, under stirring, a solution of Na₂SiO₃ (Merck, 1L = 1.35 kg) to a calcium saturated solution (a completely transparent solution of CaO, [Ca] ~18 mM). This solution was aged for up to 21 days in sealed containers inside an N₂-filled glovebox at ambient pressure and temperature. In

1 this inert environment, the supernatant was exchanged with CO₂-free water to remove
2 Na traces and to avoid carbonation during precipitation. This washing yielded a Na
3 content in the final solid phase down to 1% wt. (X-ray fluorescence, AXIOS PANalytical
4 instrument). Afterwards, the water was exchanged by ethanol, and then ethanol was
5 exchanged three times daily for 4 days to remove the water. Some minor structural
6 changes may appear due to the solvent exchange, but they are known to be negligible
7 so the obtained structures will be representative of the precipitated “frozen” C-S-H. The
8 sample was placed into an autoclave and heated up to 250°C and 72 bar. Then, the
9 ethanol was vented off under supercritical conditions, namely, releasing pressure
10 isothermally at 250°C. The complete drying process lasted 5 hours. The autoclave was
11 opened inside a nitrogen-filled glovebox and the supercritically dried C-S-H was
12 obtained. One part of the sample was weathered, that is, it was put in contact with the
13 atmosphere for 2 weeks (room temperature and ~40% RH) so the atmospheric CO₂
14 could react to form calcium carbonate.
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32

33 Two different samples were studied: the original supercritically dried C-S-H, labelled
34 scCSH, always handled with care so as to not allow it to come into contact with
35 atmospheric CO₂ to avoid weathering, and the sample that was weathered for two
36 weeks, labelled wscCSH.
37
38
39
40
41
42
43
44
45

46 Characterisation techniques

47
48
49
50

51 Phase characterisation was done by X-ray diffraction (XRD). Nitrogen
52 physisorption, small angle x-ray scattering (SAXS), energy dispersive spectrometry
53 (EDX) and scanning electron microscopy (SEM) were used for nanostructure
54 investigations. To keep the scCSH sample safe from atmospheric gases for XRD and
55
56
57
58
59
60
61
62
63
64
65

1 SAXS analyses, it was placed between two polyester films hermetically sealed and
2 mounted on sample holders inside the N₂-filled glovebox. XRD analyses were
3 performed on a diffractometer (Philips X'Pert) with Cu-K α radiation, from 5.00° to 70.00°
4 with a step of 0.05° and counting time of 80 s. SAXS experiments were performed in a
5 device with Cu-K α radiation and a 2 theta step of 0.01° (Philips X'Pert PANalytical). This
6 way, the covered q -range was 0.004 – 0.356 Å⁻¹.
7
8
9
10
11
12
13

14 Likewise, the original sample scCSH was placed inside the nitrogen physisorption
15 sample holder inside the glovebox. Nitrogen physisorption experiments (Micrometrics,
16 model ASAP2010) were made at a constant temperature of 77.35 K. Isotherm curves
17 were analysed by the Brunauer-Emmet-Teller [31] and Barret-Joyner-Halenda [32]
18 methods to obtain the specific surface area (S_{BET}) and pore size distribution (PSD),
19 respectively. The scCSH sample was degasified by heating at different temperatures
20 from 100 to 250°C, under a nitrogen flux for two hours, to explore the role of adsorbed
21 water in this nanostructure. The wscCSH sample was degasified at 100°C. SEM and
22 EDX were performed using a SEM-FEG (Hitachi S480) with an acceleration voltage of
23 2kV. The time of contamination due to atmospheric gases was minimised to <15 s, as
24 the sample was mounted on the SEM sample holder inside the glove box. Thereby, the
25 scCSH sample was in contact with the atmosphere only for the time it took to be placed
26 inside the SEM vacuum chamber and to pump down the system.
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47

48 **Results and Discussion**

49
50
51
52

53 Once the supercritical drying process was finished and the autoclave was opened
54 inside the nitrogen-filled glovebox, an extremely fine and volatile fluffy powder was
55 obtained. The XRD analyses of this scCSH powder (Figure 1) showed the presence of
56
57
58
59
60
61
62
63
64
65

1 broad weak peaks of poorly crystallized tobermorite (PDF file: 00-029-0331)
2 characteristic of C-S-H. No phase other than tobermorite was precipitated, that is, no
3 portlandite (calcium hydroxide) nor jennite, nor calcium carbonate phases were
4 observed. On the other hand, the weathering of the wscCSH was firstly confirmed by
5 XRD. In Figure 2, the x-ray diffraction pattern shows the presence of different calcium
6 carbonate polymorphs, calcite (PDF number: 00-001-0837) and aragonite (PDF
7 number: 01-071-2396), together with some resting tobermorite. The precipitation of
8 aragonite was already observed in C-S-H samples that were carbonated with no extra
9 water [33], similar to our carbonation conditions where only atmospheric humidity is
10 wetting the sample. Thus, in two weeks, the weathering of the original C-S-H was not
11 completed, given the presence of resting tobermorite.

12 The nanostructure of the scCSH was researched first by nitrogen physisorption.
13 With a gentle degasifying procedure, at $T = 100^{\circ}\text{C}$ for 2h, similar specific surface areas
14 $S_{\text{BET}} = 447 \text{ m}^2/\text{g}$ and t-Plot external surface $S_{\text{tPlot}} = 433 \text{ m}^2/\text{g}$ were measured. All the
15 structural features of the different experiments are summarised in Table 1. This
16 measured surface area was significantly higher (~20% or more) than others reported for
17 synthetic C-S-H, tobermorite, or hydrated cement pastes [1, 13, 34], typically between
18 $30 \text{ m}^2/\text{g}$ and $378 \text{ m}^2/\text{g}$. Therefore, the actual C-S-H structure that exists in the aqueous
19 media after hydration of the cement and prior to drying presents higher specific surface
20 than those typically observed by conventional procedures. Consequently, hydrated
21 cements will be more reactive than theoretically expected. A pore volume of 0.913
22 cm^3/g and a wide pore size distribution (PSD) was obtained, with a constant mesopore
23 population between 10 nm and 40 nm (Figure 3, top). Then, a monotonic increase in the
24 pore size population from 10 nm towards lower radii was observed, increasing very
25 rapidly below 5 nm, but without any well-defined pore size peak. In other words, this

1 PSD showed the presence of two levels of porosity: an important pore population below
2 5 nm formed by the packing of the elemental structural elements, and another important
3 mesopore population formed by their hierarchical arrangement. The PSD can be
4 explained by randomly arranged particles forming two different hierarchical levels.
5
6 Nevertheless, no well-defined typical pore radius was observed (no peak is observed),
7 indicating a very heterogeneous population of particle sizes and shapes. The elemental
8 building blocks forming C-S-H that have been reported in the literature as microcrystals
9 with sizes around ~5 nm [18, 35] were also present in this supercritically dried sample,
10 forming the observed porosity below 5 nm. Therefore, they were not affected by the
11 drying process and structural differences between the conventionally dried and
12 supercritically dried C-S-H have to be explained in terms of changes on higher structural
13 hierarchical levels.
14
15
16
17
18
19
20
21
22
23
24
25
26
27

28
29 Considering the skeleton density $\rho_{sk} = 2.4 \text{ g/cm}^3$ similar to tobermorite, the
30 maximum specific surface area that could be obtained would be $\sim 500 \text{ m}^2/\text{g}$, close to that
31 measured in the scCSH. Therefore, the conventional drying process induces shrinkage
32 of the globules formed by the arrangement of the elemental building blocks by bringing
33 them together, but not shrinkage of the building blocks themselves. In addition, a bulk
34 density of $\rho_{bulk} = 0.75 \text{ g/cm}^3$ and a porosity $P = 68.7\%$ could be derived for the scCSH.
35
36 This density is lower than the density of the C-S-H found in hydrated cements, between
37 1.4 – 2.0 g/cm^3 [1, 23], indicating that the obtained supercritically dried C-S-H could be
38 a frozen initial stage of the common C-S-H, prior to structure maturing and shrinkage
39 produced by conventional drying.
40
41
42
43
44
45
46
47
48
49
50
51
52

53 The role of the adsorbed water in the C-S-H nanostructure was researched by
54 changing the degasifying temperature. Nitrogen physisorption experiments were
55 performed on the original C-S-H degasified at 175°C and 250°C, in addition to 100°C
56
57
58
59
60
61
62
63
64
65

1 (discussed before). The structural parameters obtained with different degasifying
2 temperatures are summarised in Table 1, and plotted versus degassing temperature in
3 Figure 3, bottom. Instead of an increase in the specific surface area due to the release
4 of interstitial water, a significant decrease of this parameter was observed, indicating
5 shrinkage of the structure. Typical C-S-H structural models [7-9, 13, 18] have always
6 considered a certain amount of low-bonded interstitial or intraglobular water, adsorbed
7 or encapsulated among the basic building blocks of the structure. These results indicate
8 that releasing this water leads to the collapse of the structure, showing the structural
9 effects of the drying process of these nanostructured samples. This way, the specific
10 surface area S_{BET} decreases to 360 m²/g at a degassing temperature of 175°C and to
11 282 m²/g at 250°C. Moreover, supercritical drying of the C-S-H did not provoke this
12 collapse of the structure, and it was kept invariable up to the degassing process. The
13 porous volume presented a similar behaviour to specific surface area, supporting the
14 idea of shrinkage of the structure. However, the hierarchical distribution of the pores
15 does not disappear despite the shrinkage, and the three PSD curves for the three
16 different temperatures show constant shape (Figure 3, top), with a slight decrease in
17 the pore population below 5 nm with degassing at 175 °C, followed by a decrease of the
18 pore population between 10 and 30 nm when rising temperature up to 250 °C.

19 On the other hand, the weathered sample presented much lower specific surface
20 area values than any of the original samples (Table 1). Carbonation of C-S-H yields
21 calcium carbonate crystals and silica by-products. The silica by-product is an
22 amorphous silica gel with a high specific surface area and nanometric particle size, but
23 the calcium carbonate crystals, as aragonite or calcite, are expected to form micrometric
24 crystals with very low specific surface area values, thus decreasing the value of the
25 entire sample. Finally, the relative decrease of the pore volume was significantly lower,
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

indicating a larger average particle size but more spread out thanks to the contribution of the silica gel.

The scanning electron microscopy micrographs of the scCSH sample showed a random arrangement of flake-like or sheet-like structures, typical of tobermorite (Figure 4, top). The size of these flakes was quite heterogeneous, circa 20 nm wide and 200 nm long. This flake-like morphology has been associated to outer product (or low density) C-S-H [10] in coherence with the derived bulk density values discussed before. Thus, using this synthesis route and this drying procedure, synthetic low density C-S-H could be precipitated. In addition, some thin stick morphologies around 400 nm long and 20 nm thick could also be seen (upper left corner of Figure 4, top, and Figure 4, bottom). These stick morphologies have been previously reported in samples synthesised at 170°C [36]. So, the presence of stick-like morphologies could be an artefact due to the heat-treatment of the supercritical drying process.

The different morphologies of the weathering by-products can be seen in Figures 5, 6 and 7. In Figure 5, branched calcite microcrystals can be seen instead of typical rhombohedral calcite crystals. The absence of silica on these microcrystals (confirmed by EDX) supported this identification. The size of the crystals indicated a small specific surface area value, so the disappearance of C-S-H flakes and the precipitation of these large calcite crystals decreased the bulk specific surface area of the sample. In Figure 6, a branch of calcium carbonate sticks is shown. This morphology has been associated with aragonite [37]. In the background of Figures 5 and 6, remaining C-S-H flakes can be observed, showing the incomplete carbonation of C-S-H, so the mere exposure to atmospheric CO₂ under room conditions yielded a partially carbonated sample. Finally, in Figure 7, the silica by-product is shown. It precipitated as a hierarchical arrangement of pseudo-spherical particles. In this figure, 200 nm sized aggregates of silica particles

1 are shown, but smaller structural elements (< 50 nm) similar to those sizes previously
2 reported [24] can also be seen. EDX tests were made on these arrangements to
3 measure the calcium-to-silica ratio, and to discard other phases than silica. The
4 obtained values of Ca/Si = 0.40 ± 0.04 supports the identification of this phases as the
5 silica by-product. Therefore, the precipitation of this amorphous silica by-product
6 contributes to maintaining high specific surface area values of the weathered sample,
7 and a small average pore radius as well (15.8 nm), typically formed by the aggregation
8 of elemental silica particles.
9

10
11
12
13
14
15
16
17
18
19 The structural features of the scCSH and those changes due to weathering were
20 researched by SAXS as well [38]. The obtained intensities are plotted in Figure 8. First,
21 the absence of a well-defined Guinier range in the scCSH was remarkable and
22 indicated the absence of a well-defined size and shape of scatterers. The shape of the
23 curve indicated a very heterogeneous particle size and shape distribution. Nevertheless,
24 there was a change in the slope of the log-log plot, and the $q_1^{crossover}$ value indicated a
25 typical size of the scatterers of 3.2 nm. In this case, considering Babinet's Principle,
26 scattering may be caused by the pores among the elemental nanocrystalline building
27 blocks usually characterised as ~5 nm size [18, 35]. In addition, the scattering curve of
28 the original sample increased its intensity towards low q -values, revealing the existence
29 of larger (> 100 nm) typical sizes of the scatterers, which may correspond to the size of
30 the flakes. However, the covered q -range in these experiments was not sufficient to
31 resolve this large structural feature. Both linear regimes of the log-log plot of the
32 scattering curve covered much less than one decade, so the slope of these regimes
33 could not be consistently associated to any fractal description.
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54

55
56 On the other hand, the intensity curve of the wscCSH sample showed a Guinier
57 range at low q -values, with a derived Guinier's radius of 14.3 nm (28.6 nm particle size),
58
59
60
61
62
63
64
65

1 similar to the characteristic size of 29.6 nm derived from the $q_2^{crossover}$. These new
2 structural elements that appear after the weathering process are identified with silica by-
3 product particles (Figure 7), as silica gel is usually well-described by spherical particles
4 and well-resolved by small angle scattering and Guinier's model [39, 40]. In addition, the
5 previously reported $q_1^{crossover}$ could be also observed, corresponding to the persistence
6 of some ~3.2 nm sized scatterers among the resting nanocrystalline building blocks, as
7 the C-S-H had not been completely weathered.
8
9
10
11
12
13
14
15
16
17
18

19 **Conclusions**

20
21
22
23
24 The synthetic C-S-H sample dried by the supercritical drying process presented a
25 greater specific surface area and pore volume than the conventionally dried C-S-H. The
26 differences between conventionally and supercritically dried CSH are explained in terms
27 of the shrinkage of the structure due to conventional drying. In this regard, the reactive
28 surface of the C-S-H when in an aqueous paste was ~20% larger than that usually
29 measured in conventionally dried C-S-H.
30
31
32
33
34
35
36
37
38

39 The exposure of the sample to atmospheric CO₂ under room conditions is enough
40 to carbonate the sample, but 2 weeks of weathering yielded a partially carbonated
41 sample. SEM images and XRD analysis confirmed the precipitation of calcite and
42 aragonite. Finally, the hierarchical distribution of the precipitated silica gel by-product,
43 with ~28 nm typical particle size arranged in globules of ~200 nm size was observed.
44
45
46
47
48
49
50
51
52

53 **Acknowledgements**

54 The authors are grateful to the Consejería de Innovación Ciencia y Empresa of the
55 Junta de Andalucía (Spain) for supporting this work with the annual grant TEP115. This
56
57
58
59
60
61
62
63
64
65

work was possible thanks to the technical staff of the Instituto de Ciencia de Materiales de Sevilla (ICMS, CSIC-US). VMF thanks the CSIC for financial support through the JAE-Doc programme.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

References

- 1 Taylor HFW (1997) Cement Chemistry. Thomas Telford Publishing, London.
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9
- 10
- 11 2 Barlet-Gouédard V, Rimmelé G, Porcherie O, Quisel N, Desroches J (2009) Int J
- 12
- 13 Greenh Gas Control 3:206
- 14
- 15
- 16
- 17
- 18
- 19
- 20
- 21 3 Jaramillo P, Griffin WM, McCoy ST (2009) Environ Sci Technol 43(21):8027
- 22
- 23
- 24
- 25
- 26
- 27
- 28
- 29
- 30 4 Rimmelé G, Varlet-Gouédard V, Porcherie O, Goffé B, Brunet F (2008) Cem Concr
- 31
- 32 Res 38:1038
- 33
- 34
- 35
- 36
- 37
- 38
- 39
- 40
- 41
- 42 5 See for example: GRASP project (<http://www.grasp-co2.eu>) or CO2Sink project
- 43
- 44
- 45
- 46
- 47
- 48
- 49
- 50
- 51
- 52
- 53
- 54
- 55
- 56
- 57
- 58
- 59
- 60
- 61
- 62
- 63
- 64
- 65
- 66
- 67
- 68
- 69
- 70
- 71
- 72
- 73
- 74
- 75
- 76
- 77
- 78
- 79
- 80
- 81
- 82
- 83
- 84
- 85
- 86
- 87
- 88
- 89
- 90
- 91
- 92
- 93
- 94
- 95
- 96
- 97
- 98
- 99
- 100
- 101
- 102
- 103
- 104
- 105
- 106
- 107
- 108
- 109
- 110
- 111
- 112
- 113
- 114
- 115
- 116
- 117
- 118
- 119
- 120
- 121
- 122
- 123
- 124
- 125
- 126
- 127
- 128
- 129
- 130
- 131
- 132
- 133
- 134
- 135
- 136
- 137
- 138
- 139
- 140
- 141
- 142
- 143
- 144
- 145
- 146
- 147
- 148
- 149
- 150
- 151
- 152
- 153
- 154
- 155
- 156
- 157
- 158
- 159
- 160
- 161
- 162
- 163
- 164
- 165
- 166
- 167
- 168
- 169
- 170
- 171
- 172
- 173
- 174
- 175
- 176
- 177
- 178
- 179
- 180
- 181
- 182
- 183
- 184
- 185
- 186
- 187
- 188
- 189
- 190
- 191
- 192
- 193
- 194
- 195
- 196
- 197
- 198
- 199
- 200
- 201
- 202
- 203
- 204
- 205
- 206
- 207
- 208
- 209
- 210
- 211
- 212
- 213
- 214
- 215
- 216
- 217
- 218
- 219
- 220
- 221
- 222
- 223
- 224
- 225
- 226
- 227
- 228
- 229
- 230
- 231
- 232
- 233
- 234
- 235
- 236
- 237
- 238
- 239
- 240
- 241
- 242
- 243
- 244
- 245
- 246
- 247
- 248
- 249
- 250
- 251
- 252
- 253
- 254
- 255
- 256
- 257
- 258
- 259
- 260
- 261
- 262
- 263
- 264
- 265
- 266
- 267
- 268
- 269
- 270
- 271
- 272
- 273
- 274
- 275
- 276
- 277
- 278
- 279
- 280
- 281
- 282
- 283
- 284
- 285
- 286
- 287
- 288
- 289
- 290
- 291
- 292
- 293
- 294
- 295
- 296
- 297
- 298
- 299
- 300
- 301
- 302
- 303
- 304
- 305
- 306
- 307
- 308
- 309
- 310
- 311
- 312
- 313
- 314
- 315
- 316
- 317
- 318
- 319
- 320
- 321
- 322
- 323
- 324
- 325
- 326
- 327
- 328
- 329
- 330
- 331
- 332
- 333
- 334
- 335
- 336
- 337
- 338
- 339
- 340
- 341
- 342
- 343
- 344
- 345
- 346
- 347
- 348
- 349
- 350
- 351
- 352
- 353
- 354
- 355
- 356
- 357
- 358
- 359
- 360
- 361
- 362
- 363
- 364
- 365
- 366
- 367
- 368
- 369
- 370
- 371
- 372
- 373
- 374
- 375
- 376
- 377
- 378
- 379
- 380
- 381
- 382
- 383
- 384
- 385
- 386
- 387
- 388
- 389
- 390
- 391
- 392
- 393
- 394
- 395
- 396
- 397
- 398
- 399
- 400
- 401
- 402
- 403
- 404
- 405
- 406
- 407
- 408
- 409
- 410
- 411
- 412
- 413
- 414
- 415
- 416
- 417
- 418
- 419
- 420
- 421
- 422
- 423
- 424
- 425
- 426
- 427
- 428
- 429
- 430
- 431
- 432
- 433
- 434
- 435
- 436
- 437
- 438
- 439
- 440
- 441
- 442
- 443
- 444
- 445
- 446
- 447
- 448
- 449
- 450
- 451
- 452
- 453
- 454
- 455
- 456
- 457
- 458
- 459
- 460
- 461
- 462
- 463
- 464
- 465
- 466
- 467
- 468
- 469
- 470
- 471
- 472
- 473
- 474
- 475
- 476
- 477
- 478
- 479
- 480
- 481
- 482
- 483
- 484
- 485
- 486
- 487
- 488
- 489
- 490
- 491
- 492
- 493
- 494
- 495
- 496
- 497
- 498
- 499
- 500
- 501
- 502
- 503
- 504
- 505
- 506
- 507
- 508
- 509
- 510
- 511
- 512
- 513
- 514
- 515
- 516
- 517
- 518
- 519
- 520
- 521
- 522
- 523
- 524
- 525
- 526
- 527
- 528
- 529
- 530
- 531
- 532
- 533
- 534
- 535
- 536
- 537
- 538
- 539
- 540
- 541
- 542
- 543
- 544
- 545
- 546
- 547
- 548
- 549
- 550
- 551
- 552
- 553
- 554
- 555
- 556
- 557
- 558
- 559
- 560
- 561
- 562
- 563
- 564
- 565
- 566
- 567
- 568
- 569
- 570
- 571
- 572
- 573
- 574
- 575
- 576
- 577
- 578
- 579
- 580
- 581
- 582
- 583
- 584
- 585
- 586
- 587
- 588
- 589
- 590
- 591
- 592
- 593
- 594
- 595
- 596
- 597
- 598
- 599
- 600
- 601
- 602
- 603
- 604
- 605
- 606
- 607
- 608
- 609
- 610
- 611
- 612
- 613
- 614
- 615
- 616
- 617
- 618
- 619
- 620
- 621
- 622
- 623
- 624
- 625
- 626
- 627
- 628
- 629
- 630
- 631
- 632
- 633
- 634
- 635
- 636
- 637
- 638
- 639
- 640
- 641
- 642
- 643
- 644
- 645
- 646
- 647
- 648
- 649
- 650
- 651
- 652
- 653
- 654
- 655
- 656
- 657
- 658
- 659
- 660
- 661
- 662
- 663
- 664
- 665
- 666
- 667
- 668
- 669
- 670
- 671
- 672
- 673
- 674
- 675
- 676
- 677
- 678
- 679
- 680
- 681
- 682
- 683
- 684
- 685
- 686
- 687
- 688
- 689
- 690
- 691
- 692
- 693
- 694
- 695
- 696
- 697
- 698
- 699
- 700
- 701
- 702
- 703
- 704
- 705
- 706
- 707
- 708
- 709
- 710
- 711
- 712
- 713
- 714
- 715
- 716
- 717
- 718
- 719
- 720
- 721
- 722
- 723
- 724
- 725
- 726
- 727
- 728
- 729
- 730
- 731
- 732
- 733
- 734
- 735
- 736
- 737
- 738
- 739
- 740
- 741
- 742
- 743
- 744
- 745
- 746
- 747
- 748
- 749
- 750
- 751
- 752
- 753
- 754
- 755
- 756
- 757
- 758
- 759
- 760
- 761
- 762
- 763
- 764
- 765
- 766
- 767
- 768
- 769
- 770
- 771
- 772
- 773
- 774
- 775
- 776
- 777
- 778
- 779
- 780
- 781
- 782
- 783
- 784
- 785
- 786
- 787
- 788
- 789
- 790
- 791
- 792
- 793
- 794
- 795
- 796
- 797
- 798
- 799
- 800
- 801
- 802
- 803
- 804
- 805
- 806
- 807
- 808
- 809
- 810
- 811
- 812
- 813
- 814
- 815
- 816
- 817
- 818
- 819
- 820
- 821
- 822
- 823
- 824
- 825
- 826
- 827
- 828
- 829
- 830
- 831
- 832
- 833
- 834
- 835
- 836
- 837
- 838
- 839
- 840
- 841
- 842
- 843
- 844
- 845
- 846
- 847
- 848
- 849
- 850
- 851
- 852
- 853
- 854
- 855
- 856
- 857
- 858
- 859
- 860
- 861
- 862
- 863
- 864
- 865
- 866
- 867
- 868
- 869
- 870
- 871
- 872
- 873
- 874
- 875
- 876
- 877
- 878
- 879
- 880
- 881
- 882
- 883
- 884
- 885
- 886
- 887
- 888
- 889
- 890
- 891
- 892
- 893
- 894
- 895
- 896
- 897
- 898
- 899
- 900
- 901
- 902
- 903
- 904
- 905
- 906
- 907
- 908
- 909
- 910
- 911
- 912
- 913
- 914
- 915
- 916
- 917
- 918
- 919
- 920
- 921
- 922
- 923
- 924
- 925
- 926
- 927
- 928
- 929
- 930
- 931
- 932
- 933
- 934
- 935
- 936
- 937
- 938
- 939
- 940
- 941
- 942
- 943
- 944
- 945
- 946
- 947
- 948
- 949
- 950
- 951
- 952
- 953
- 954
- 955
- 956
- 957
- 958
- 959
- 960
- 961
- 962
- 963
- 964
- 965
- 966
- 967
- 968
- 969
- 970
- 971
- 972
- 973
- 974
- 975
- 976
- 977
- 978
- 979
- 980
- 981
- 982
- 983
- 984
- 985
- 986
- 987
- 988
- 989
- 990
- 991
- 992
- 993
- 994
- 995
- 996
- 997
- 998
- 999
- 1000

82:064203

1
2
3 17 Thomas JJ, Jennings HM, Allen AJ (1998) Cem Concr Res 28:897
4

5
6 18 Allen AJ, Thomas JJ, Jennings HM (2007) Nat Materials 6:311
7

8
9 19 Blinc R, Lahajnar G, Zummer S (1988) Phys Rev B 38:2873
10

11
12 20 Thomas JJ, Allen AJ, Jennings HM (2008) J Am Ceram Soc 91:3362
13

14
15 21 Skinner LB, Chae SR, Benmore CJ, Wenk HR, Monteiro PJM (2010) Phys Rev Lett
16
17 104:195502
18

19
20 22 Manzano H, Ayuela A, Dolado JS (2007) J Comp. Aided Mater Des 14:45
21

22
23 23 Gonzalez-Teresa R, Morales-Florez V, Manzano H, Dolado JS (2010) Materiales de
24
25 construccion 60:7
26

27
28 24 Häussler F, Palzer S, Eckart A, Hoell A (2002) Appl Phys A 74:s1124
29

30
31 25 Morales-Florez V, Brunet F (2012) J Mater Sci 47:764
32

33
34 26 Garbev K, Stemmermann P, Black L, Breen C, Yarwood J (2007) J Am Ceram Soc
35
36 90:900
37

38
39 27 Black L, Garbev K, Gee I (2008) Cem Concr Res 38:745
40

41
42 28 Johannesson B, Utgennant P (2001) Cem Concr Res 31:925
43

44
45 29 Kistler S. Coherent Expanded-Aerogels (1932) J Phys Chem 36(1):52
46

47
48 30 Sugiyama D, Fujita T (2006) Cem Concr Res 36:227
49

50
51 31 Brunauer S, Emmett PH, Teller E (1938) J Am Chem Soc 60:309
52

53
54 32 Barret EP, Joyner LG, Halenda PP (1951) J Am Chem Soc 73:373
55

56
57 33 Shtepenko O, Hills C, Brough A, Thomas M (2006) Chem Eng J 118:107
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

34 Siauciunas R, Rupsyte E, Kitrys S, Galeckas V (2004) Coll And Surf A 244:197

35 Xu Z, Viehland D (1996) Phys Rev Lett 77:952

36 Rossler C, Stark J, Steiniger F, Tichelaar W (2006) J Am. Ceram. Soc **89**:627

37 Gobac ZZ, Posilović H, Bermanec V (2009) Geologia Croatica 62(3):201

38 Glatter O, Kratky O (1982) Small Angle X-Ray Scattering. Academic Press, London

39 De la Rosa-Fox N, Morales-Flórez V, Toledo-Fernández JA, Piñero M, Esquivias L, Keiderling U (2008) J Sol-Gel Sci and Tech 45:245

40 Woignier T, Reynes J, Hafidi Alaoui A, Beurroies I, Phalippou J (1998) J of Non-Cryst Solids 241:45

TABLES AND FIGURE CAPTIONS

Tables

Table 1. Nitrogen physisorption results for the scCSH and the wscCSH degasified at different temperatures. For derived bulk density and porosity values, tobermorite density has been considered as the skeleton density.

Figures

Figure 1. X-ray diffraction pattern (Cu-K α radiation) of the scCSH.

Figure 2. X-ray diffraction pattern (Cu-K α radiation) of the wscCSH.

Figure 3. Top, pore size distributions of the scCSH obtained for different degassing temperatures. Bottom, dependence of texture parameters (specific surface area S_{BET} and porous volume V_p) on degassing temperature for the scCSH sample.

Figure 4. Scanning electron micrographies of the scCSH sample.

Figure 5. Scanning electron micrography of the wscCSH sample.

Figure 6. Calcium carbonate microcrystals of the wscCSH observed by SEM.

Figure 7. Silica gel by-product observed in the weathered wscCSH sample.

1
2 Figure 8. SAXS intensities of both scCSH and wscCSH samples. The intensities were
3
4 normalised for comparison purposes.
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Table 1

Degassing temperature (°C)	S _{BET} (m ² /g)	S _{tPlot} (m ² /g)	<Rp> nm	V _p (cm ³ /g)	ρ _{bulk} (g/cm ³)	Porosity (%)
Original sample						
100	447	433	7.5	0.913	0.752	68.7
175	360	329	6.5	0.686	0.907	62.2
250	282	277	6.8	0.567	1.017	57.6
Weathered sample						
100	166	160	15.8	0.587	0.996	58.5

Figure 1

[Click here to download high resolution image](#)

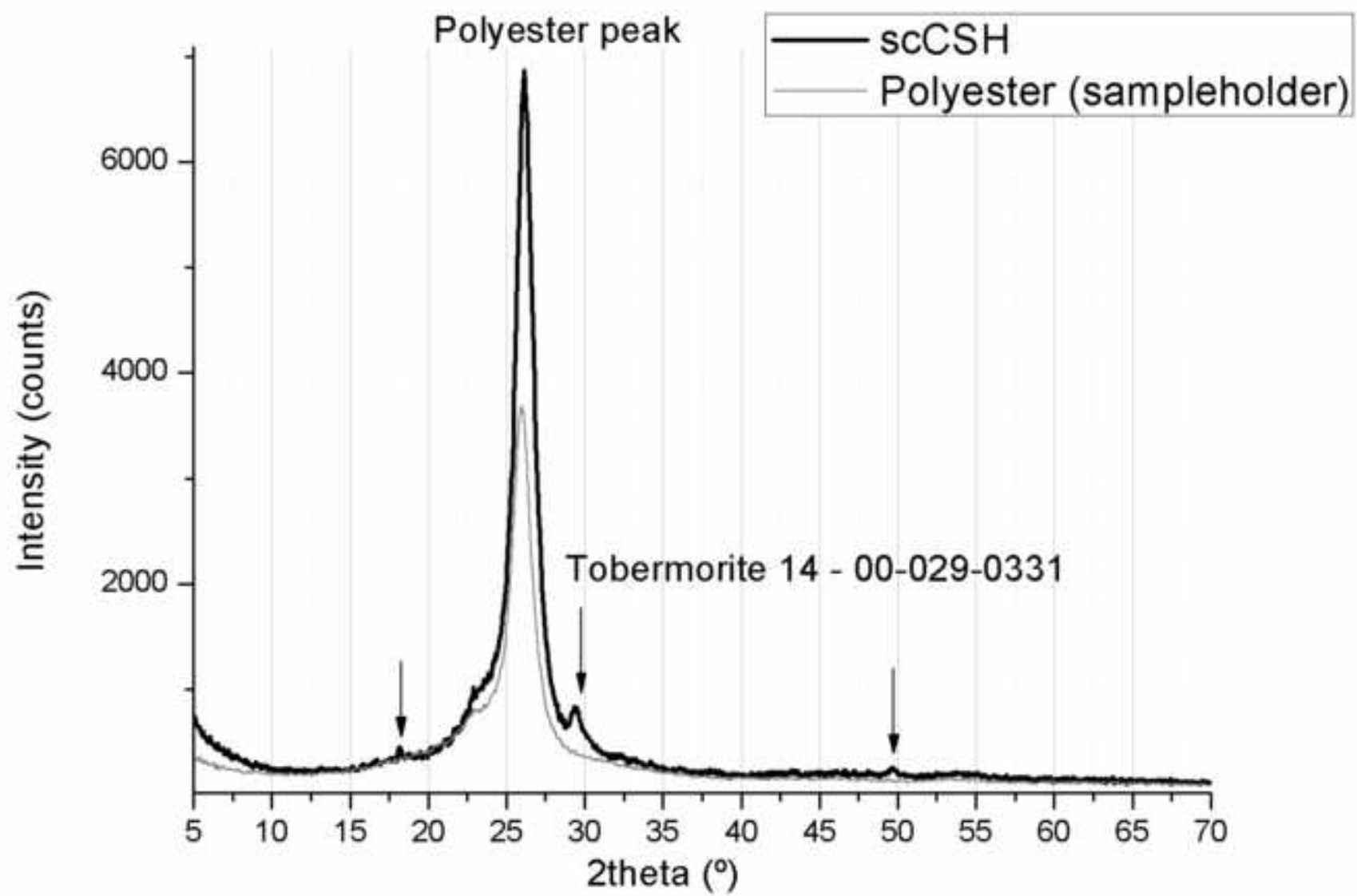


Figure 2

[Click here to download high resolution image](#)

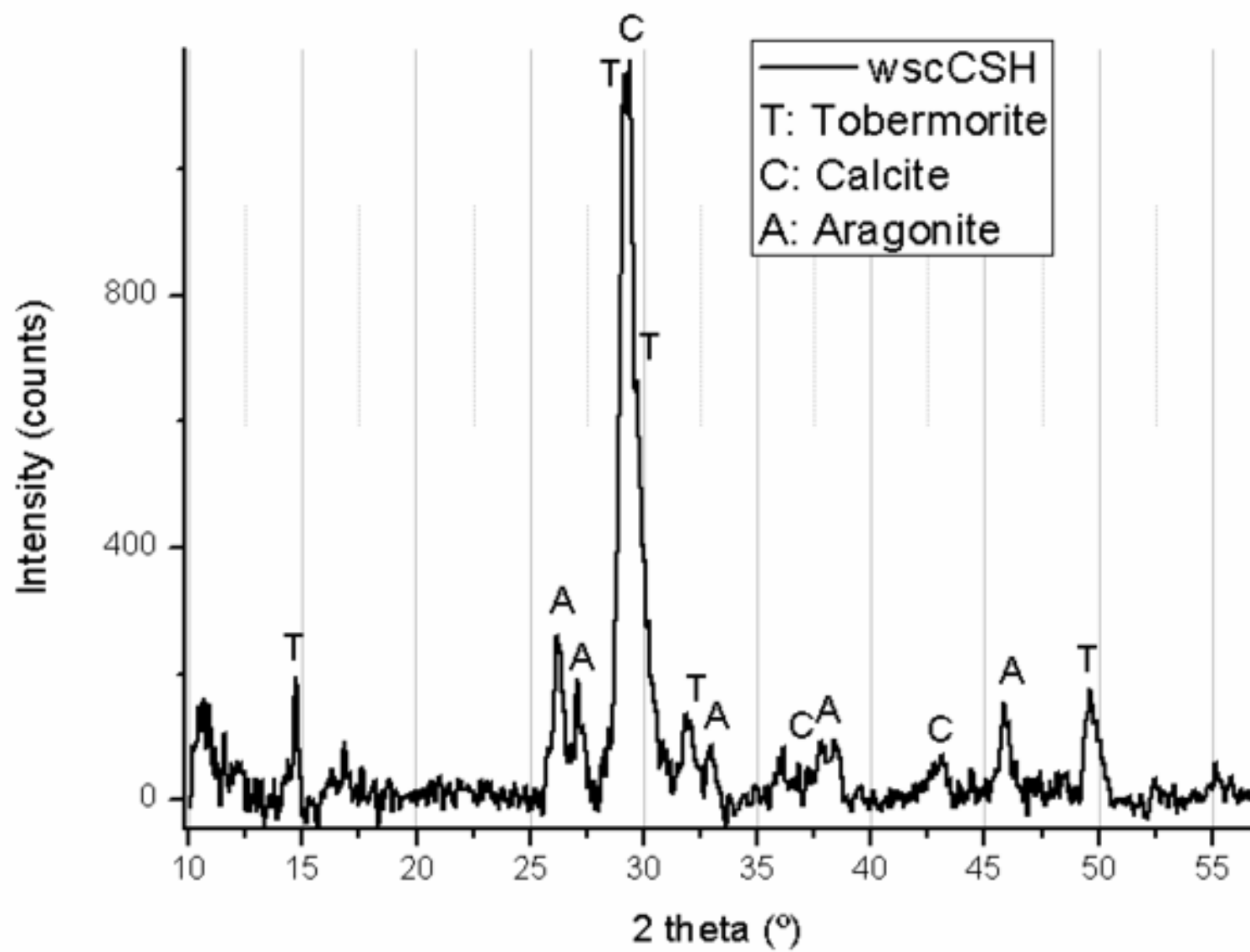


Figure 3
[Click here to download high resolution image](#)

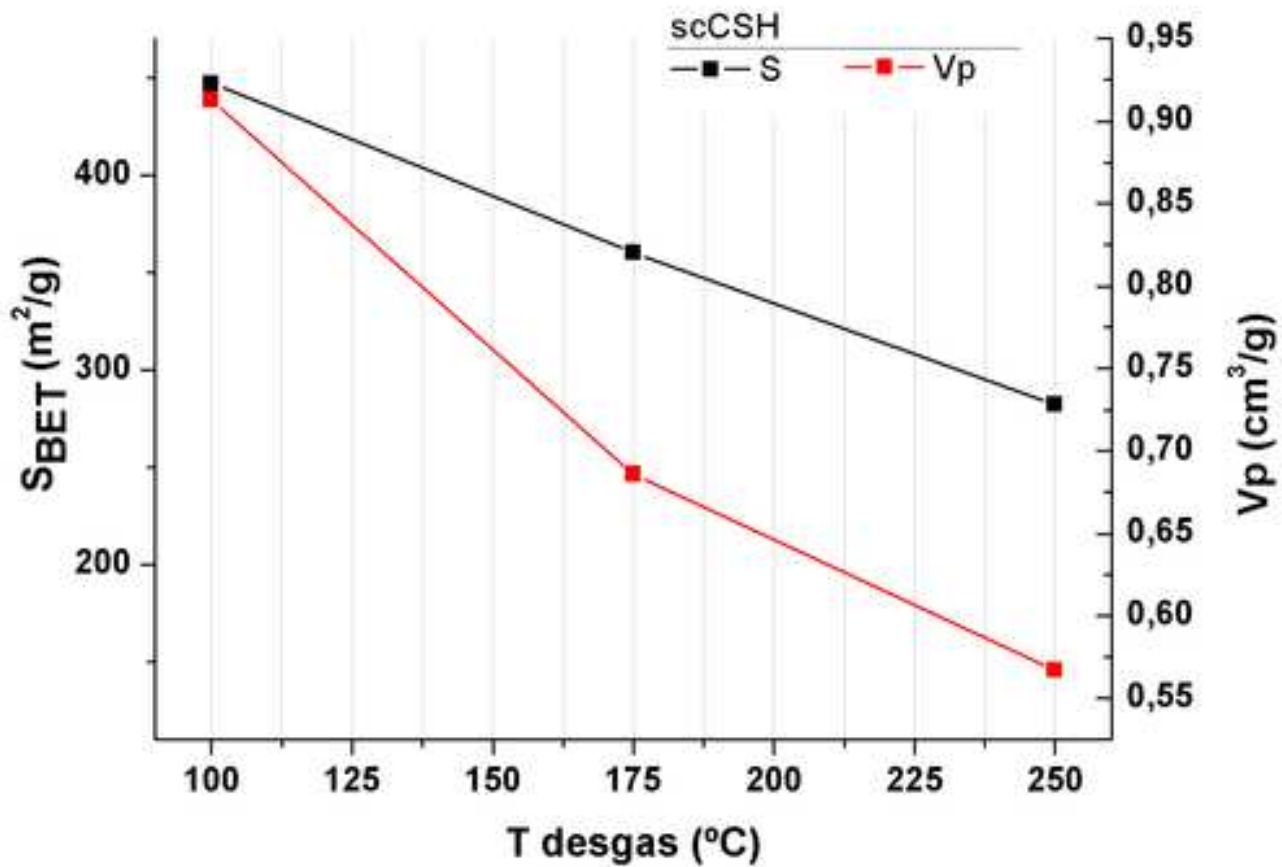
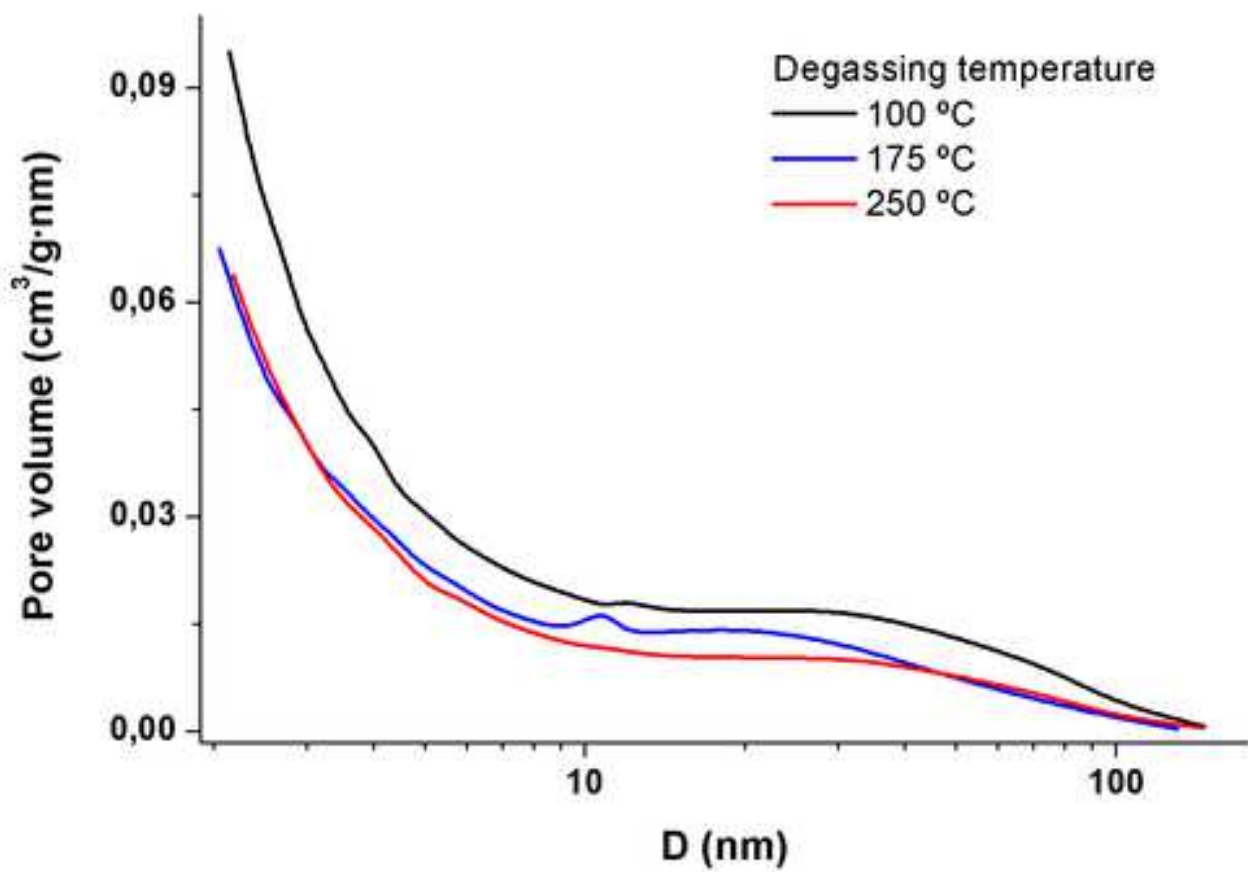


Figure 4
[Click here to download high resolution image](#)

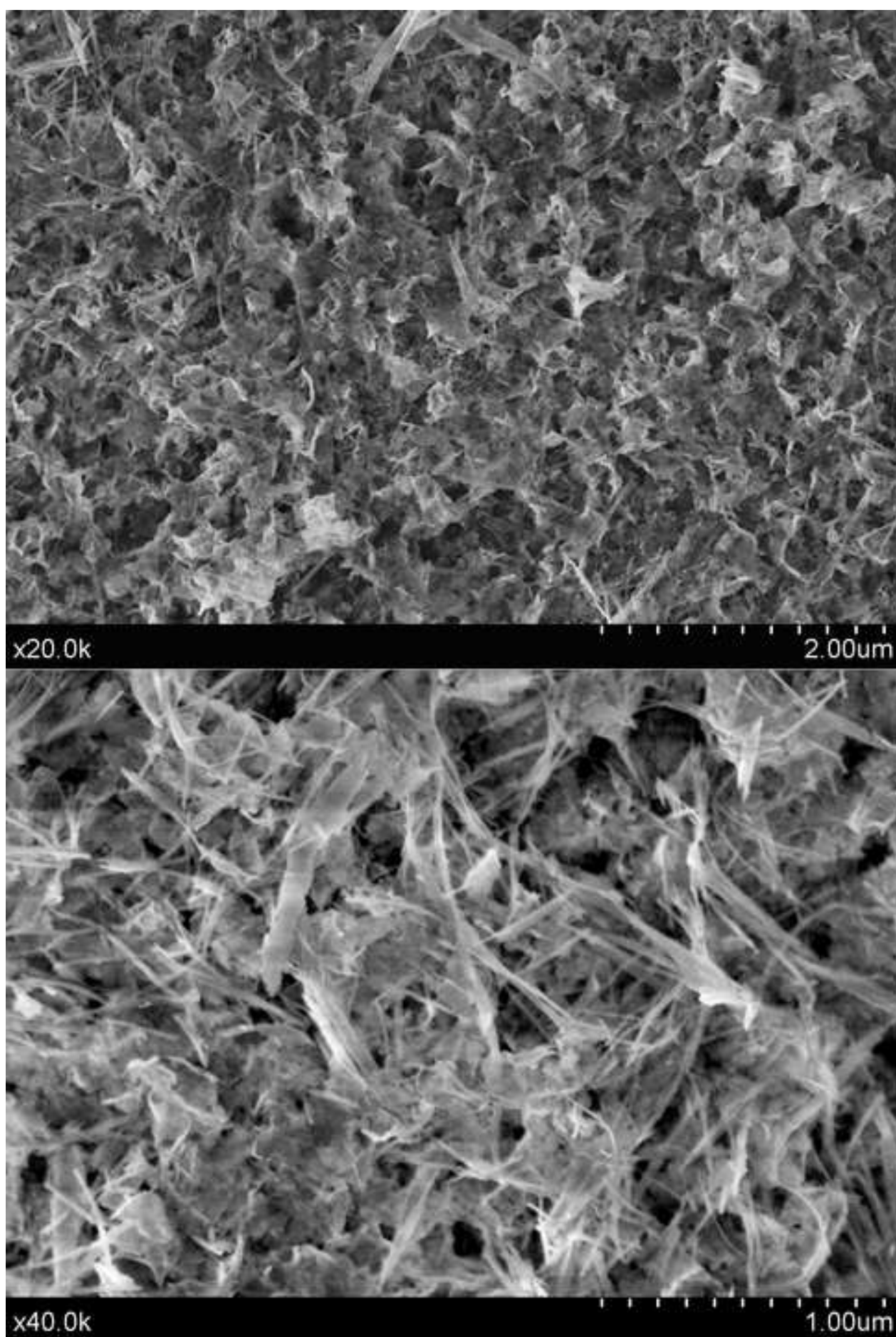


Figure 5
[Click here to download high resolution image](#)

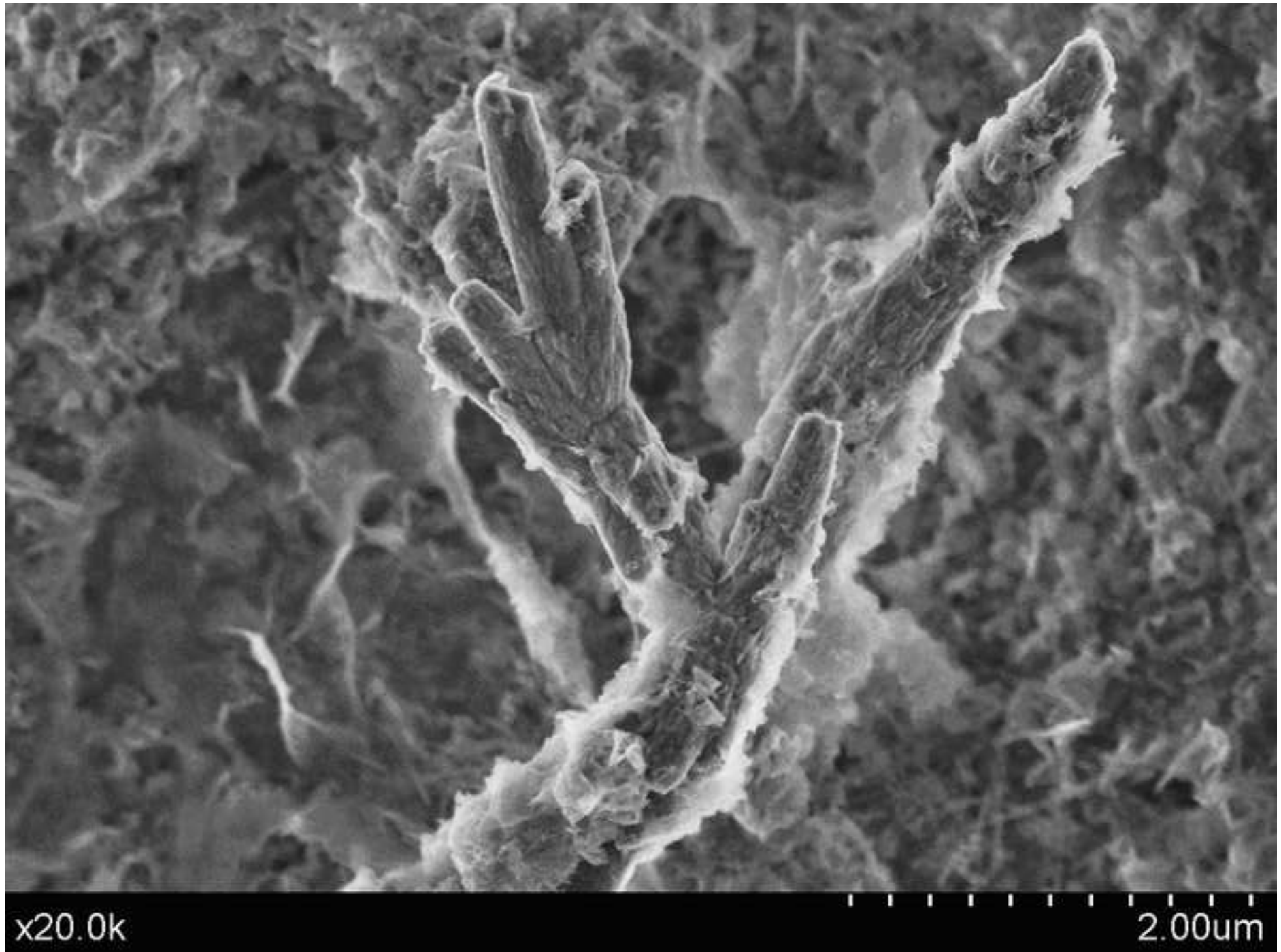


Figure 6
[Click here to download high resolution image](#)

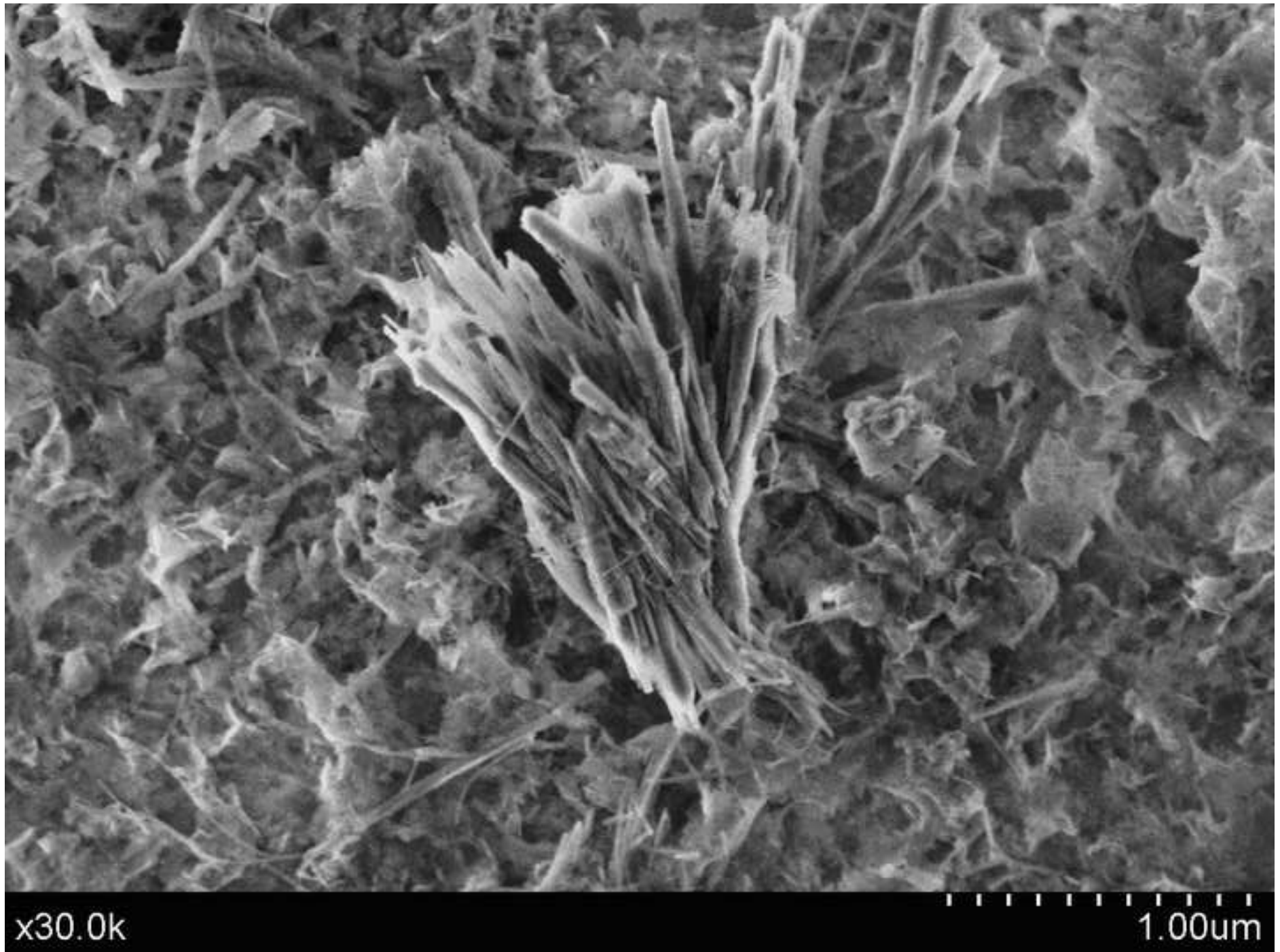


Figure 7

[Click here to download high resolution image](#)

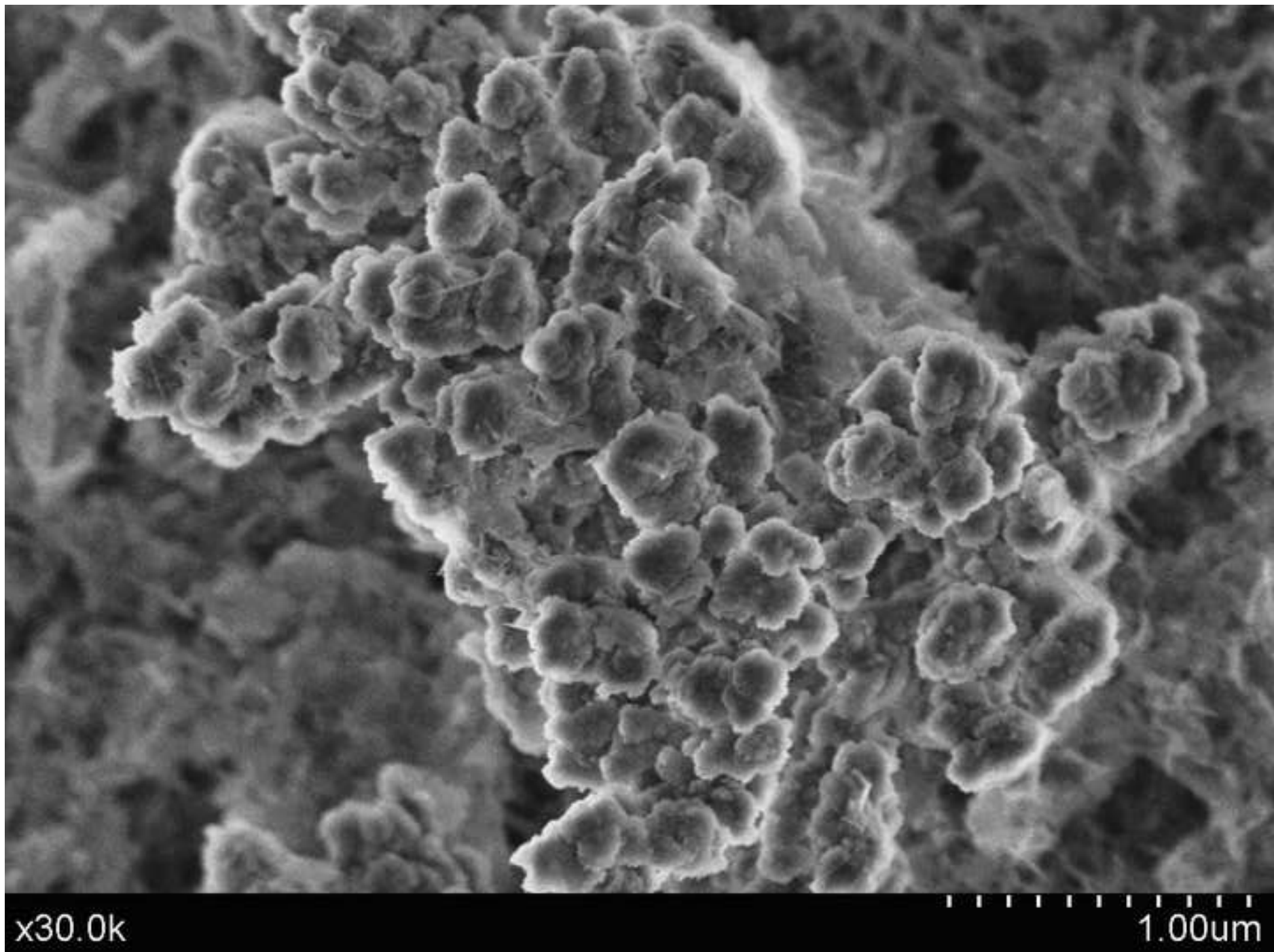


Figure 8

[Click here to download high resolution image](#)

