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Dark fermentation process as pretreatment for a sustainable denaturation of asbestos containing wastes

This is a pre-print of the following article

Original Citation:

Dark fermentation process as pretreatment for a sustainable denaturation of asbestos containing wastes / Spasiano, Danilo. - In: JOURNAL OF HAZARDOUS MATERIALS. - ISSN 0304-3894. - STAMPA. - 349:(2018), pp. 45-50. [10.1016/j.jhazmat.2018.01.049]

Availability:

This version is available at <http://hdl.handle.net/11589/122842> since: 2021-03-17

Published version

DOI:10.1016/j.jhazmat.2018.01.049

Publisher:

Terms of use:

(Article begins on next page)

Manuscript Number: HAZMAT-D-17-04478

Title: Dark fermentation process as pretreatment for a sustainable denaturation of asbestos containing wastes

Article Type: Research Paper

Keywords: dark fermentation; glucose; asbestos; hydrogen; hydrothermal treatment.

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Abstract: The present study represents the first attempt to an eco-sustainable bio-thermal denaturation of a real cement-asbestos sample. At this purpose, an Eternit slate was detoxified by a treatment train based on a dark fermentation process followed by a hydrothermal phase, which led to the complete degradation of the chrysotile fibers. During the biological pretreatment, the glucose, the biodegradable substrate adopted in this study, was converted in biogas rich in H₂ and volatile fatty acids (VFA). The latter caused the dissolution of all the Ca based compounds and the solubilization of 50% brucite layers of chrysotile fibers contained in the Eternit sample suspended in the bioreactor (5 g L⁻¹). XRD analysis of the solids contained in the effluents of the DF process highlighted the disappearance of the peaks related to the chrysotile fibers. However, since a complete destruction of all the asbestos fibers could not be proved, a hydrothermal treatment was carried out at 100 °C and room pressure with the aim of dissolving the brucite layers still present in solution. At this purpose, a complete destruction of chrysotile fibers was achieved by means of a 24 h hydrothermal process carried out with the addition of 1.25 g L⁻¹ sulfuric acid.

DICATECh – Politecnico di Bari
Via Orabona, 4, 70125, Bari, Italy

Prof. Gerasimos Lyberatos

Editor of Journal of Hazardous Materials

Dear Prof. Lyberatos

please find enclosed a copy of the original manuscript:

“Dark fermentation process as pretreatment for a sustainable denaturation of asbestos containing wastes”

by Danilo Spasiano.

Number of words: 3750.

This study shows the first attempt to an eco-sustainable bio-thermal denaturation of a real cement asbestos sample. At this purpose, an Eternit slate sample was denaturated by a biological anaerobic pretreatment, the dark fermentation, followed by a hydrothermal treatment. The adoption of the dark fermentation as pretreatment plays a key role in the whole treatment train since it leads to the conversion of a biodegradable substrate (glucose, in this study) into volatile fatty acids, which decreased the acid consumption during the hydrothermal treatment. In particular, compared to what has already been reported in the literature, the sulfuric acid consumption has been halved. Moreover, the glucose biodegradation operated by the dark fermentation process leads to the production of a biogas rich in molecular hydrogen which could be used as energy source during the hydrothermal phase.

I believe that this topic is of high interest to the readership of Journal of Hazardous Materials, since it deals with the treatment of a hazardous waste, which is attracting the attention of the scientific community and the political world.

This is an original manuscript not submitted elsewhere. I confirm that the present manuscript has been prepared in compliance with the Ethics in Publishing Policy as described in the Guide for Authors of Journal of Hazardous Materials.

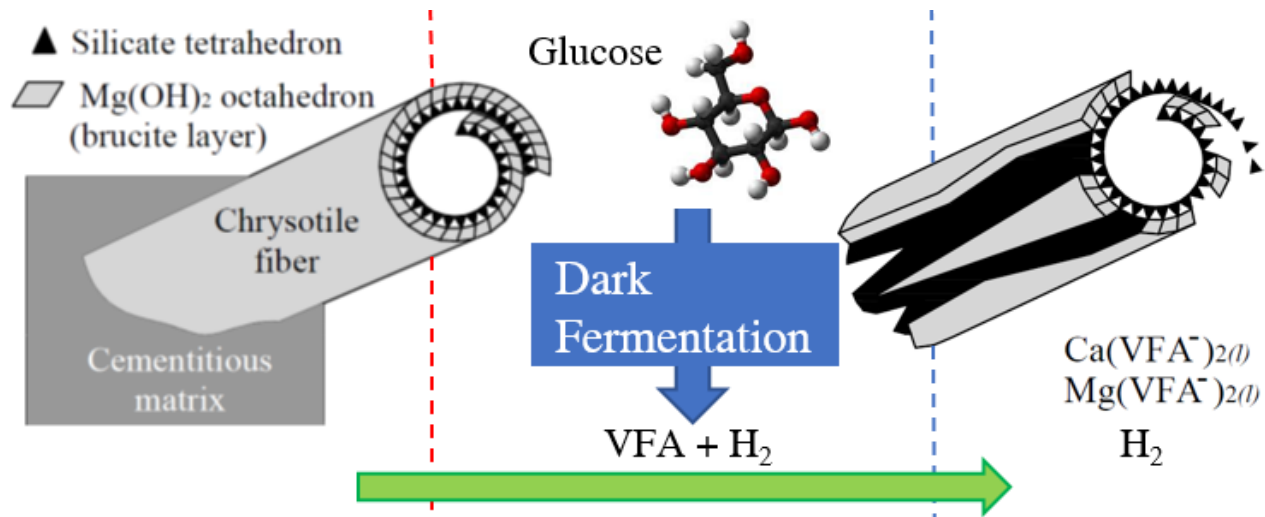
I look forward to receiving your editorial response in due course.

Yours sincerely

Danilo Spasiano, PhD

Statement of novelty

The main novelty of this study consists in the adoption of a cheap and sustainable treatment train based on by a biological process, the dark fermentation, followed by a hydrothermal treatment for the denaturation of a real cement-asbestos sample. Moreover, for the first time, the complete denaturation of all the asbestos fibers was proved not only by XRD analysis of the suspended solids after the process, but also by the analysis of the Mg^{2+} concentration in the solution. At the best of the Author knowledge, nobody has ever proposed or published something like this.



Highlights

- Dark fermentation (DF) may be an ecofriendly tool for cement-asbestos hydrothermal denaturation
- The VFA generated during the DF led to a complete dissolution of the cement matrix of 5 g/L Eternit
- After the DF, also 50% of the brucite layer of the chrysotile initially suspended was dissolved
- During the DF process $465.4 \text{ mmol L}^{-1}$ of bio- H_2 were produced
- Compared to what was previously reported, the use of acids during the hydrothermal phase was halved

Dark fermentation process as pretreatment for a sustainable denaturation of asbestos containing wastes

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Abstract

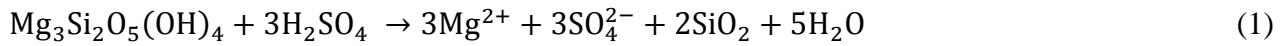
The present study represents the first attempt to an eco-sustainable bio-thermal denaturation of a real cement-asbestos sample. At this purpose, an Eternit slate was detoxified by a treatment train based on a dark fermentation process followed by a hydrothermal phase, which led to the complete degradation of the chrysotile fibers. During the biological pretreatment, the glucose, the biodegradable substrate adopted in this study, was converted in biogas rich in H₂ and volatile fatty acids (VFA). The latter caused the dissolution of all the Ca based compounds and the solubilization of 50% brucite layers of chrysotile fibers contained in the Eternit sample suspended in the bioreactor (5 g L⁻¹). XRD analysis of the solids contained in the effluents of the DF process highlighted the disappearance of the peaks related to the chrysotile fibers. However, since a complete destruction of all the asbestos fibers could not be proved, a hydrothermal treatment was carried out at 100 °C and room pressure with the aim of dissolving the brucite layers still present in solution. At this purpose, a complete destruction of chrysotile fibers was achieved by means of a 24 h hydrothermal process carried out with the addition of 1.25 g L⁻¹ sulfuric acid.

1. Introduction

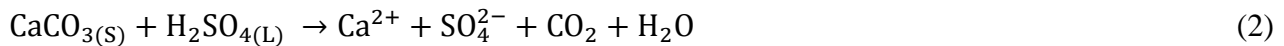
The treatment and the management of asbestos containing wastes (ACW) is increasingly attracting the attention of the scientific community and the political world. Indeed, during the last two decades, many processes, aimed to the asbestos denaturation, were proposed as alternative to the ACW landfilling. In particular, vitrification by plasma gun [1,2] or Joule heating [3], thermal [4-6], mechano-chemical [7,8] and chemical [9-12] treatments have been shown to be effective at destroying asbestos fibers by generating non-harmful, and sometime reusable, by-products. As a consequence of these new scientific findings, on January the 30th, 2013, the European Parliament not only has encouraged the development of action plans for asbestos removal and management, but also promoted and supported “*research into, and technologies using, eco-compatible alternatives, and to secure procedures, such as the inertisation of waste-containing asbestos, to deactivate active asbestos fibers and convert them into materials that do not pose public health risks*” [13]. The reason why the EU Parliament has undertaken these actions is not only related to the $1.07 \cdot 10^6$ deaths per year due to asbestos related illness [14-16], but also to asbestos airbones release from the damaging of asbestos containing products after natural and made-man disasters. Indeed, the generation of large volumes of asbestos containing debris, occurred after the 2005 Katrina hurricane, the 2011 Katrina hurricane, and the terroristic attack to the World Trade Center in 2001, generated environmental and public health problems, making the disaster management even more difficult [17-19].

Unfortunately, the innovative treatments, briefly outlined above, have been adopted only few times at industrial scale because of their high cost, generally related to the large consumption of energy and/or reagents. In fact, the only two plants that can treat ACW are the Inertam and GeoMelt[®], which adopt the vitrification treatment by plasma gun and Joule heating respectively [1, 20]. In particular, the Inertam plant, opened in 1999 in France, can treat $8 \cdot 10^3$ tons ACW per year and produces, as an end-product, a rocklike material, which is sold as quartz and basalt replacement in

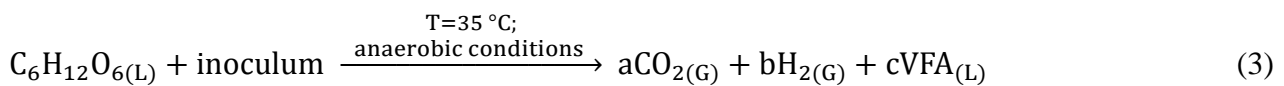
the construction industry for 10 € ton⁻¹. On the other hand, due to the high process temperature (1600 °C) the minimum cost for the ACW treatment in this plant is 1.0·10³ € ton⁻¹. Consequently, with the aim of reducing the costs related to the energy consumption, it has been recently proposed a thermochemical process, which can treat 5 g of a cement asbestos compound (CAC) suspended in 10 mL solution containing 2.5 g of sulfuric acid (5 N) at 100 °C for 24 h [21]. This process is effective because the chrysotile fibers (Mg₃Si₂O₅(OH)₄), the most used asbestos fibrous silicate minerals, when suspended into an acidic solution undergo to a denaturation process consisting in the dissolution of the brucite layer with a consequent release of Mg²⁺ ions (1) [22-24]:



However, CACs, which generally contain only 8-15 %_{w/w} of asbestos fibers, are characterized by the presence of calcium compounds, as calcium carbonate (CaCO₃), portlandite (Ca(OH)₂) and calcium silicates, that compete with asbestos fibers in the reaction with the acids (2) [21]:



Consequently, a large amount of acids is consumed for the dissolution of the CAC cement matrix. For this reason, a recently published paper suggested the adoption of the dark fermentation (DF), a biological anaerobic process, of biodegradable substrates as pretreatment for the hydrothermal denaturation of the asbestos fibers contained in the CAC. In particular, the DF of glucose was proven to produce H₂ and VFA (3) [25, 26], which can dissolve the cement matrix of 5 g L⁻¹ fiber-glass reinforced composite (4), simulating a CAC, suspended into the solution [27].



As a result, the adoption of the DF of biodegradable compounds, as pretreatment of a hydrothermal phase, seems to be a promising solution to reduce the costs of the hydrothermal CAC denaturation because: i) it produces bio-H₂, a renewable source of energy, which could be used to reduce the energy necessary for the hydrothermal process; ii) it produces a large quantity of organic acids, as

1 acetic, butyric, lactic, valeric, and propionic acid, which may reduce the consumption of reagents
2 during the hydrothermal phase; iii) since agro-food wastes could be used as biodegradable
3 compounds during the DF pretreatment, the whole process would be able to simultaneously treat
4 two types of wastes.
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9 However, the treatment of real CAC with the DF/hydrothermal treatment train has never been
10 carried out. To this purpose, in this paper the adoption of the glucose DF, which would simulate a
11 waste molasses, a by-product deriving from sugar refinery [28,29], as pretreatment of real CAC
12 sample has been attempted for the first time.
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22 **2. Materials and methods**

23 **2.1. Materials**

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25 HPLC grade acetonitrile was purchased from Carlo Erba. Sulfuric acid (98%), nitric acid (70%),
26 hydrochloric acid (35%), hydrogen peroxide (30%), and anhydrous glucose (99.5%) were
27 purchased from Sigma Aldrich. All reagents and organic solvents were used as received. In all the
28 experiments, distilled water was used as solvent.
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37 The digestate withdrawal from the mesophilic anaerobic digestion (AD) plant of the dairy farm
38 “Davide Colangelo” located in Capaccio (Salerno, Italy) was used for the preparation of DF
39 inoculum. In particular, the total solids (TS), volatile solids (VS) and the pH of the AD sludge were
40 equal to 48.15 g L⁻¹, 25.9 g L⁻¹ and 7.8 respectively. The Mg²⁺ and Ca²⁺ concentration were equal to
41 302 ppm and 1298 ppm respectively. Moreover, no VFAs were detected.
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49 A company handling hazardous waste provided the Eternit slate sample. In particular, the Eternit
50 sample, was stored, cleaned, and milled with the procedure elsewhere described [21]. Finally, the
51 sample was sieved to get a particle size below 2.0 mm, dried at 105 °C, and characterized by SEM
52 (Figure 1a-b), EDX (Table 1) and XRD analysis (Figure 1c). In particular, the EDX mapping of the
53 main elements of the CAC sample, reported in Figure 3S, highlights an accumulation of magnesium
54 on the chrysotile fibers due to the presence of the brucite layer.
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1 With regard to the calcium and magnesium concentrations in the CAC sample, they were also
2 validated by means of a wet digestion procedure, according to the EPA method 3050 [30]. In
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4 agreement with the EDX analysis, the weight percentages of Ca and Mg evaluated with the EPA
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6 standard method were 29.9 and 3.0 respectively.
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10 11 **2.2. DF experimental apparatus**

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14 The DF tests were carried out with an inoculum obtained after a thermal treatment of the anaerobic
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16 digestion sludge, which inhibited the methanogenic bacteria. In particular, the digestate was heated
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18 in oven for 1 h at 105 °C as reported elsewhere [31].
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22 In a 2.0 L air tight borosilicate glass bottle GL 45 (Shott Duran, Germany), 500 mL of inoculum
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24 were mixed with 500 mL distilled water ($V_{\text{sol}} = 1.0 \text{ L}$). With the aim of adopting the same substrate
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26 to inoculum ratio (F/M) used in the previous investigation, 31 g L⁻¹ of glucose were added to the
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28 solution [27]. Afterwards, the bottle was closed with a screw cap equipped with two sampling pipes
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30 for the withdrawal of gaseous and liquid samples. In particular, once the bottles was closed, 30 min
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32 pure nitrogen bubbling was carried out by using the liquid sample pipe as entry of the gas and the
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34 gas sample pipe as exit, with the aim of guarantee the anaerobic conditions. The DF reactor was
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36 immersed into a thermostatic bath at $35 \pm 1 \text{ °C}$ and magnetically stirred at 370 rpm. Once the
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38 production of hydrogen reached the plateau, the cap was removed and, under nitrogen atmosphere,
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40 5.0 g L⁻¹ dried CAC sample and other 31 g L⁻¹ glucose were added into the solutions. Since large
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42 volumes of bio-gas were expected during the biological process, a 10 L air tight glass bottle GH 45
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44 (Shott Duran, Germany) was used to withdrawal and measure the volume of bio-gas. At this
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46 purpose, the 10 L bottle, filled with water, was closed with a screw cap equipped with three pipes: i)
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48 the first was connected to the gas sampling tube of the biological reactor with a quick compression
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50 fitting; ii) the second was used for the gas sampling; iii) the third, which reaches the bottom of the
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52 10 L bottle, was used to ensure the water outlet from the bottle (Figure 1S). In particular, the
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54 volume of biogas produced during the test was measured by disconnecting the quick compression
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1 fitting after closing the upstream and downstream valves. Afterwards, the 10 L and 2 L bottles were
2 connected to a eudiometer to measure the volume of bio-gas under pressure. The whole produced
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4 biogas was considered as the sum of the volumes measured with the eudiometer and the volume of
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6 water necessary to refill the 10 L bottle.
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10 11 **2.3. Hydrothermal experimental apparatus**

12 At the end of the DF process, 100 mL of the solution, deriving from the energetically stirred (800
13 rpm) DF solution, were added in a 2-neck round bottom flask closed with a 60 cm Graam condenser
14 cooled with tap water. The solution was magnetically stirred and heated as illustrated in Figure 2S.
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16 The samples were withdrawn with a 5 mL syringe, centrifuged, filtered, diluted and finally
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18 analyzed.
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29 **2.4. Analytical methods**

30 Both Ca^{2+} and Mg^{2+} dissolved ion concentrations were quantified by atomic absorption
31 spectrometry using a Varian Model 55B SpectrAA (F-AAS) equipped with a flame (acetylene/air)
32 and a deuterium lamp for background correction.
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38 Biogas composition was evaluated with a Varian Star 3400 gas chromatograph equipped with
39 ShinCarbon ST 80/100 column and a thermal conductivity detector. Argon was used as carrier gas
40 with 1.4 bar front and rear end pressure.
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45 The concentrations of the organic acids were measured with a high pressure liquid chromatography.
46 Specifically, a Dionex LC 25 Chromatography Oven equipped with a polymer-based cation-
47 exchanger column (Metrohm Metrosep Organic Acids - 250/7.8) and a Dionex AD25 Absorbance
48 Detector were combined with a gradient pump (Dionex GP 50), eluting the samples with sulphuric
49 acid 0.5 mM at the flow rate of 0.7 mL min^{-1} .
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1 SEM images and EDX analysis of the solid samples were carried out with an electron microscope
2 FESEM-EDX Carl Zeiss Sigma 300 VP. In particular, the samples were fixed on aluminum stubs
3 and then sputtered with gold with a Sputter Quorum Q150.
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7 The samples were analyzed for their mineralogy using a PANalytical X'Pert Pro diffractometer, at
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9 40 kV and 40 mA, using Cu K α radiation, with divergence slit of 0.5, spinner revolution 1 mm s⁻¹
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12¹. The apparatus was equipped with a solid-state detector (X'Celerator) covering an angle of 2.1°
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14 and integrates the diffracted intensity as it scans. The powders were scanned in the range 3–70° 2 θ .
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17 In particular, the SEM, EDX, and XRD characterization of the solids suspended into the DF
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19 solution and the hydrothermal effluents were carried out on the solid phase deriving from the
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21 centrifugation (4500 rpm at 4 °C) of 50 ml samples. Before its characterization, the solid phase,
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23 having a muddy appearance, was lyophilized with a single chamber lyophilizer (Martin Christ
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25 Alpha 1-4 LSCplus) and then ground in an agate planetary ball mill.
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29 Total solids and volatile solids and COD were measured according to APHA standard methods
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31 [32]. The pH of the solution was monitored with a Hanna Instruments HI 98190 pH/ORP pH-meter.
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36 **3. Results and discussion**

37 **3.1 DF pretreatment**

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41 The start-up of the DF pretreatment consisted in the addition of 31 g of glucose in the bioreactor
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43 ($V_{\text{sol}} = 1.0$ L) in absence of the CAC sample. During this phase, lasting 65 h, the microorganisms
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45 degraded the glucose producing VFAs, which lowered the pH of the solution to 5.45, and 233.8
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47 mmol of bio-hydrogen. Afterwards, when the H₂ production reached the plateau, 5 g of CAC were
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49 added to the solution together with other 31 g of glucose. As a result, the already activated
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51 fermentative bacteria immediately started to degrade the substrate leading to an almost constant H₂
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53 production, which terminated after 62 h ($t_f = 127$ h), reaching a bio-H₂ production of 465.4 mmol
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55 (Figure 2). During the process, as reported in table 1, the VFA production raised and the pH of the
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57 solution decreased.
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As a result, after the CAC addition, it was observed the dissolution of the cement matrix and of the
brucite layer ($\text{Mg}(\text{OH})_2$) of the chrysotile fibers present in the CAC sample. Indeed, as reported in
figure 3, both Ca^{2+} (full squares) and Mg^{2+} (empty circles) dissolved ions were detected in the
solution with increasing concentrations during the treatment time. In particular, the Ca^{2+} and Mg^{2+}
concentrations were reported after deduction of their values during the DF start-up ($[\text{Ca}^{2+}]_{65\text{h}} = 649$
ppm; $[\text{Mg}^{2+}]_{65\text{h}} = 155$ ppm) and were normalized with respect to the theoretical concentrations
($[\text{Ca}^{2+}]_t = 1500$ ppm. $[\text{Mg}^{2+}]_t = 150$ ppm) calculated on the basis of the results deriving from the
CAC sample characterization. As a consequence of the dissolution of calcium and magnesium
alkaline based compounds, the pH of the solution remained in a range close to the optimal one
without the addition of expensive buffers [33,34]. Indeed, the optimal pH for the DF process should
be slightly acidic with the aim of inhibiting the methanogenic activity ($\text{pH} > 6$) and the solvent
production ($\text{pH} < 4.5$) [35,36].

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At the end of the DF pretreatment, the Ca^{2+} concentration reached the maximum value and,
consequently, all the cement matrix of the CAC sample was dissolved. Moreover, the normalized
 Mg^{2+} concentration after the DF pretreatment was equal to 0.5. This result highlighted that much of
the chrysotile denaturing process has been carried out since the structure of chrysotile fibers should
be collapsed as a consequence of the brucite layer dissolution (Figure 4). A similar phenomenon
was already observed in chrysotile-containing serpentinite rocks or asbestos cement roofs colonized
by lichens, after some years of contact time. Indeed, the products of the metabolic activity of some
species of lichens, such as *Acarospora cervina*, *Candelariella aurella*, and *Candelariella vitellina*,
are rich in oxalic acid, which extract Mg^{2+} ions from chrysotile fibers forming glushinskite, a
soluble organic salt that is leached during the rainfall events [37,38]. Likewise, the siderophores and
the chelating agents secreted by the metabolic activity of a *Bacillus mucilaginosus* culture strongly
damaged the structure of a serpentine rock, within 20-30 days contact time. Indeed, the XRD
analysis on the solids at the end of the biological treatment highlighted a strong decrease of
serpentine peak sharpness and width and an increase of amorphous contents [39].

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In this study, the comparison of XRD analysis of the suspended solids in the solution immediately after the addition of the CAC sample (65 h) and at the end of the DF process (127 h) shows the complete disappearance of peaks related to both chrysotile and calcite (Figure 5). Although the denaturation of asbestos fibers is very likely because 50% of the brucite layer of chrysotile has been dissolved and the XRD analysis do not show their presence, the complete CAC denaturation can not be demonstrated. Indeed, it is possible that the detection limit of XRD has been reached and few asbestos fibers are still present in the solution. As a matter of fact, only a complete brucite layer dissolution could prove the complete CAC denaturation. Consequently, a hydrothermal treatment is still necessary.

3.2 Hydrothermal treatment

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With the aim of dissolving the magnesium still present in the solid state at the end of the DF pretreatment, three hydrothermal treatment tests (100 °C and room pressure) were carried out by the use of sulfuric acid in a 0 - 2.5 g L⁻¹ concentration range. As reported in Figure 6, the treatment carried out in absence of sulfuric acid (empty circles) led to a further brucite layer dissolution, but 24.1% of Mg⁺² was still in solid form. Consequently, a complete CAC denaturation has not yet been proven, although it is even more likely. On the contrary, with the addition of 1.25 g L⁻¹ and 2.5 g L⁻¹ of sulfuric acid a complete dissolution of the brucite layer, or rather a complete denaturation of asbestos fibers, was achieved within 24 h and 8 h hydrothermal treatment respectively. As a consequence, it has been demonstrated that, when 1.25 g L⁻¹ of H₂SO₄ were added to the solution, a ratio [H₂SO₄]/[CAC] equal to 0.25 was enough to surely destroy all the chrysotile fibers contained in the CAC. This result represents a great improvement over what was reported by Nam et al. [21] because 50% of H₂SO₄ has been saved.

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During the DF processes, only ~30% of the theoretical amount of energy contained in the feedstock is converted in bio-hydrogen and the rest remains in solution in the form of VFA or other dissolved organic compounds [40]. At this purpose, during the hydrothermal treatment, the organic dissolved

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load, mainly constituted by the VFA produced within the DF pretreatment, remained almost unaltered. Indeed, the COD of the filtered solution withdrawn at the end of the DF process has passed from a value of 55.6 g L⁻¹ to 51.2 g L⁻¹ at the end of the hydrothermal treatment carried out with 1.25 g L⁻¹ of sulfuric acid. This aspect is very important because a so high dissolved COD may favor a final treatment, such as the anaerobic digestion or the microbial fuel cell, leading to the stabilization of sludge and to the generation of another source of energy [41,42]. This latter perspective is very interesting because it could further decrease the energetic cost of the whole CAC denaturation.

Conclusions

This study demonstrates that the DF process can be considered as a valid pretreatment for the hydrothermal processes aimed to the denaturation of CAC, since it can lead to a decrease in energy and reagents costs. Indeed, the VFA, produced during the dark fermentation of glucose in mesophilic condition, were responsible of the complete dissolution of the cement matrix and the 50% dissolution of the brucite layer constituting the chrysotile fibers initially present in the CAC, when 5 g L⁻¹ of the reference material were suspended in the solution. In addition, the 465.4 mmol L⁻¹ of bio-H₂, produced during the whole dark fermentation process, could generate a renewable source of energy supporting the hydrothermal phase. Indeed, even if at the end of the dark fermentation process the XRD did not highlighted the presence of chrysotile fibers in the solution, a hydrothermal phase at 100 °C was carried out with the aim of avoiding the presence of asbestos fibers in the effluents. At this purpose, the hydrothermal treatment was carried out both in presence and in absence of sulfuric acid. In particular, when sulfuric acid was not added to the solution, the hydrothermal treatment resulted, within 24 h, in a 75.9% magnesium dissolution, which may lead to a complete asbestos denaturation. On the other hand, a complete magnesium dissolution can be reached with a [H₂SO₄]/[CAC] ratio equal to 0.25, which is half of that previously reported.

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2 Finally, the energy balance of the whole process could be improved with a last biological process
3 aimed to convert the VFA still present in the hydrothermal effluents into another energy source.
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7 **Acknowledgements**

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10 This work was funded by Fondo di Sviluppo e Coesione 2007-2013 – APQ Ricerca Regione Puglia
11
12 “Programma regionale a sostegno della specializzazione intelligente e della sostenibilità sociale ed
13 ambientale – FutureInResearch”. Furthermore, the present investigation was carried out with the
14
15 support of Fondazione Puglia.
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23 **References**

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25
26 [1] E. Bernardo, G. Scarinci, E. Edme, U. Michon, N. Planty, Fast-Sintered Gehlenite Glass–
27
28 Ceramics from Plasma-Vitrified Municipal Solid Waste Incinerator Fly Ashes, *J. Am. Ceram. Soc.*
29
30 92(2) (2009) 528–530. DOI: 10.1111/j.1551-2916.2008.02892.x
31
32
33 [2] E. Bernardo, L. Esposito, E. Rambaldi, A. Tucci, Sintered glass ceramic articles from plasma
34
35 vitrified asbestos containing waste, *Adv. Appl. Ceram.* 110(6) (2011) 346–352. DOI:
36
37 10.1179/1743676111Y.0000000020
38
39
40 [3] F. Dellisanti, P.L. Rossi, G. Valdrè, Remediation of asbestos containing materials by Joule
41
42 heating vitrification performed in a pre-pilot apparatus, *Int. J. Miner. Process.* 91 (2009) 61–67.
43
44 DOI: 10.1016/j.minpro.2008.12.001
45
46
47 [4] A.F. Gualtieri, C. Giacobbe, L. Sardisco, M. Saraceno, M.L. Gualtieri, G. Lusvardi, C. Cavenati,
48
49 I. Zanatto, Recycling of the product of thermal inertization of cement–asbestos for various
50
51 industrial applications, *Waste Manage.* 31 (2011) 91–100. DOI: 10.1016/j.wasman.2010.07.006
52
53
54 [5] R. Kusiorowski, T. Zaremba, J. Piotrowski, Influence of the type of pre-calcined asbestos
55
56 containing wastes on the properties of sintered ceramics, *Construction and Building Materials* 106
57
58 (2016) 422–429. DOI: 10.1016/j.conbuildmat.2015.12.110
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64
65
- [6] N. Yoshikawa, K. Kashimura, M. Hashiguchi, M. Sato, S. Horikoshi, T. Mitani, N. Shinohara, Detoxification mechanism of asbestos materials by microwave treatment, *J. Hazard. Mater.* 284 (2015) 201–206. DOI: 10.1016/j.jhazmat.2014.09.030
- [7] P. Plescia, D. Gizzi, S. Benedetti, L. Camilucci, C. Fanizza, P. De Simone, F. Paglietti, Mechanochemical treatment to recycling asbestos containing waste, *Waste Manage.* 23 (2003) 209–218. DOI: 10.1016/S0956-053X(02)00156-3
- [8] F. Colangelo, R. Cioffi, M. Lavorgna, L. Verdolotti, L. De Stefano, Treatment and recycling of asbestos-cement containing waste, *J. Hazard. Mater.* 195 (2011) 391–397. DOI: 10.1016/j.jhazmat.2011.08.057
- [9] K. Yanagisawa, T. Kozawa, A. Onda, M. Kanazawa, J. Shinohara, T. Takanami, M. Shiraishi, A novel decomposition technique of friable asbestos by CHClF_2 -decomposed acidic gas, *J. Hazard. Mater.* 163 (2009) 593–599. DOI: 10.1016/j.jhazmat.2008.07.017
- [10] A. Valouma, A. Verganelaki, P. Maravelaki-Kalaitzaki, E. Gidaracos, Chrysotile asbestos detoxification with a combined treatment of oxalic acid and silicates producing amorphous silica and biomaterial, *J. Hazard. Mater.* 305 (2016) 164–170. DOI: 10.1016/j.jhazmat.2015.11.036
- [11] M. Rozalen, F.J. Huertas, Comparative effect of chrysotile leaching in nitric, sulfuric and oxalic acids at room temperature, *Chem. Geol.* 352 (2013) 134–142. DOI: 10.1016/j.chemgeo.2013.06.004
- [12] F. Turci, M. Colonna, M. Tomatis, S. Mantegna, G. Cravotto, B. Fubini, New detoxification processes for asbestos fibers in the environment, *J. Toxicol. Environ. Health A* 73 (2010) 368–377. DOI: 10.1080/15287390903442678
- [13] D. Spasiano, F. Pirozzi, Treatments of asbestos containing wastes, *J. Environ. Manage.* 204 (2017) 82–91. DOI: 10.1016/j.jenvman.2017.08.038
- [14] A.L. Frank, T.K. Joshi, The global spread of asbestos, *Ann. Glob. Health.* 80(4) (2014) 257–62. DOI: 10.1016/j.aogh.2014.09.016

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65
- [15] D. Marsili, P. Comba, Asbestos case and its current implications for global health, *Ann. Ist. Super. Sanita.* 49(3) (2013) 249–51. DOI: 10.4415/ANN_13_03_03
- [16] I. Choi, R.W. Smith, Kinetic Study of Dissolution of Asbestos Fibers in Water, *J. Colloid Interface Sci.* 40(2) 1972 253-262. DOI: 10.1016/0021-9797(72)90014-8
- [17] D.L. Brandon, V.F. Medina, A.B. Morrow, A Case History Study of the Recycling Efforts from the United States Army Corps of Engineers Hurricane Katrina Debris Removal Mission in Mississippi, *Advances in Civil Engineering*, Article ID 526256 (2011) 9 pages. DOI: 10.1155/2011/526256
- [18] K. Kashimura, T. Yamaguchi, M. Sato, S. Yoneda, T. Kishima, S. Horikoshi, N. Yoshikawa, T. Mitani, N. Shinohara, Rapid Transformation of Asbestos into Harmless Waste by a Microwave Rotary Furnace: Application of Microwave Heating to Rubble Processing of the 2011 Tohoku Earthquake, *J. Hazard. Toxic Radioact. Waste* 19(3) (2015) 04014041–8. DOI: 10.1061/(ASCE)HZ.2153-5515.0000249
- [19] P.J. Landrigan, P.J. Liroy, G. Thurston, G. Berkowitz, L.C. Chen, S.N. Chillrud, S.H. Gavett, P.G. Georgopoulos, A.S. Geyh, S. Levin, F. Perera, S.M. Rappaport, C. Small, NIEHS World Trade Center Working Group, Health and Environmental Consequences of the World Trade Center Disaster, *Environ. Health Perspect.* 112(6) (2004) 731–739. DOI: 10.1289/ehp.6702
- [20] K.G. Finucane, L.E. Thompson, T. Abuku, H. Nakauchi, Treatment of asbestos waste using the Geomelt Vitrification Process, WM2008 Conference, February 24-28, Phoenix, AZ, Abstract #8261, (2008) 1–10.
- [21] S.M. Nam, S. Jeong, H. Lim, Thermochemical destruction of asbestos-containing roofing slate and the feasibility of using recycled waste sulfuric acid, *J. Hazard. Mater.* 65 (2014) 151–157. DOI: 10.1016/j.jhazmat.2013.11.004
- [22] G. Alexander, M. Maroto-Valer, P. Gafarova-Aksoy, Evaluation of reaction variables in the dissolution of serpentine for mineral carbonation, *Fuel* 86 (2007) 273–281. DOI: 10.1016/j.fuel.2006.04.034

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62
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64
65
- [23] S. Tier, H. Revitzer, S. Eloneva, C.J. Fogelholm, R. Zevenhoven, Dissolution of natural serpentinite in mineral and organic acids, *Int. J. Miner. Process.* 83 (2007) 36–46. DOI: 10.1016/j.minpro.2007.04.001
- [24] M. Fujishige, R. Sato, A. Kuribara, I. Karasawa, A. Kojima, CaCl₂ addition effect and melt formation in low-temperature decomposition of chrysotile with CaCO₃, *J. Ceram. Soc. Jpn.* 114(10) (2006) 844–848. DOI: 10.2109/jcersj.114.844
- [25] A. Ghimire, V. Luongo, L. Frunzo, F. Pirozzi, P.N.L. Lens, G. Esposito, Continuous biohydrogen production by thermophilic dark fermentation of cheese whey: Use of buffalo manure as buffering agent, *Int. J. Hydrogen Energy* 42(8) (2017) 4861–4869. DOI: 10.1016/j.ijhydene.2016.11.185.
- [26] H. Argun, S. Dao, Bio-hydrogen production from waste peach pulp by dark fermentation: Effect of inoculum addition, *Int. J. Hydrogen Energy* 42(4) (2017) 2569–2574. DOI: 10.1016/j.ijhydene.2016.06.225
- [27] D. Spasiano, V. Luongo, A. Petrella, M. Alfè, F. Pirozzi, U. Fratino, A.F. Piccinni, Preliminary study on the adoption of dark fermentation as pretreatment for a sustainable hydrothermal denaturation of cement-asbestos composites, *J. Clean. Prod.* 166 (2017) 172–180. DOI: 10.1016/j.jclepro.2017.08.029
- [28] D. Yan, Y. Lu, Y.F. Chen, Q. Wu, Waste molasses alone displaces glucose-based medium for microalgal fermentation towards cost-saving biodiesel production, *Bioresour. Technol.* 102(11) (2011) 6487–6493. DOI: 10.1016/j.biortech.2011.03.036
- [29] K. Xu, P. Xu, Efficient production of L-lactic acid using co-feeding strategy based on cane molasses/glucose carbon sources, *Bioresour. Technol.* 153 (2014) 23–29. DOI: 10.1016/j.biortech.2013.11.057
- [30] US EPA, Acid Digestion of Sediments, Sludges, and Soils. EPA Method 3050B, 1996.

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52
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57
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59
60
61
62
63
64
65
- [31] A. Ghimire, L. Frunzo, L. Pontoni, G. d'Antonio, P.N.L. Lens, G. Esposito, F. Pirozzi, Dark fermentation of complex waste biomass for biohydrogen production by pretreated thermophilic anaerobic digestate, *J. Environ. Manag.* 152 (2015) 43–48. DOI: 10.1016/j.jenvman.2014.12.049
- [32] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association/American Water Works Association/Water Environment Federation, Washington DC, 1998.
- [33] I. Shizas, D.M. Bagley, Fermentative hydrogen production in a system using anaerobic digester sludge without heat treatment as a biomass source, *Water Sci. Technol.* 52(1-2) (2005) 139-144.
- [34] H.H. Fang, H. Liu, Effect of pH on hydrogen production from glucose by a mixed culture, *Bioresour. Technol.* 82(1) (2002) 87-93. DOI: 10.1016/S0960-8524(01)00110-9
- [35] S.K. Khanal, W.H. Chen, L. Li, S. Sung, Biological hydrogen production: effects of pH and intermediate products, *Int. J. Hydrogen Energy* 29(11) (2004) 1123-1131. DOI: 10.1016/j.ijhydene.2003.11.002
- [36] G.L. Tang, J. Huang, Z.J. Sun, Q.Q. Tang, C.H. Yan, G.Q. Liu, Biohydrogen production from cattle wastewater by enriched anaerobic mixed consortia: influence of fermentation temperature and pH, *J. Biosci. Bioeng.* 106(1) (2008) 80-87. DOI: 10.1263/jbb.106.80
- [37] S.E. Favero-Longo, F. Turci, M. Tomatis, D. Castelli, P. Bonfante, M.F. Hochella, R. Piervittori, B. Fubini, Chrysotile asbestos is progressively converted into a non-fibrous amorphous material by the chelating action of lichen metabolites, *J. Environ. Monit.* 7 (2005) 764–766. DOI: 10.1039/b507569f
- [38] S.E. Favero-Longo, D. Castelli, B. Fubini, R. Piervittori, Lichens on asbestos–cement roofs: Bioweathering and biocovering effects, *J. Hazard. Mater.* 162 (2009) 1300–1308. DOI: 10.1016/j.jhazmat.2008.06.060
- [39] M. Yao, B. Lian, H.H. Teng, Y. Tian, X. Yang, Serpentine Dissolution in the Presence of Bacteria *Bacillus mucilaginosus*, *Geomicrobiol. J.* 30(1) (2013) 72–80. DOI: 10.1080/01490451.2011.653087

1 [40] H.S. Shin, D.H. Kim, 2010 A two-stage fermentation process converting waste and wastewater
2 to hydrogen and methane. In: H.H.P. Fang (Eds.), Environmental Anaerobic Technology
3 Applications and New Developments, Imperial College Press, London, 2010, pp. 345–358. ISBN:
4 978-1-84816-542-7
5
6
7
8

9 [41] B. Ruggeri, T. Tommasi, G. Sassi, Energy balance of dark anaerobic fermentation as a tool for
10 sustainability analysis, Int. J. Hydrogen Energy 35(19) (2010) 10202–10211. DOI:
11 10.1016/j.ijhydene.2010.08.014
12
13
14
15

16 [42] K.R.J. Perera, B. Ketheesan, V. Gadhamshetty, N. Nirmalakhandan, Fermentative biohydrogen
17 production: evaluation of net energy gain, Int. J. Hydrogen Energy 35(22) (2010) 12224-12233.
18 DOI: 10.1016/j.ijhydene.2010.08.037
19
20
21
22
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Element	Concentration (g/kg)
C	64.6
O	490.3
Mg	31.0
Al	13.1
Si	82.1
K	4.9
Ca	300.7
Fe	13.2

Table 1

t	Formic Acid	Acetic Acid	Butyric Acid	Lactic Acid	pH
(h)	(ppm)	(ppm)	(ppm)	(ppm)	
0	0	0	0	0	7,89
65	1494	1886	6367	1611	5,45
74	965	1830	7066	1822	5,58
89	902	1991	9213	3312	5,19
127	895	2064	15163	8463	4,74

Table 2

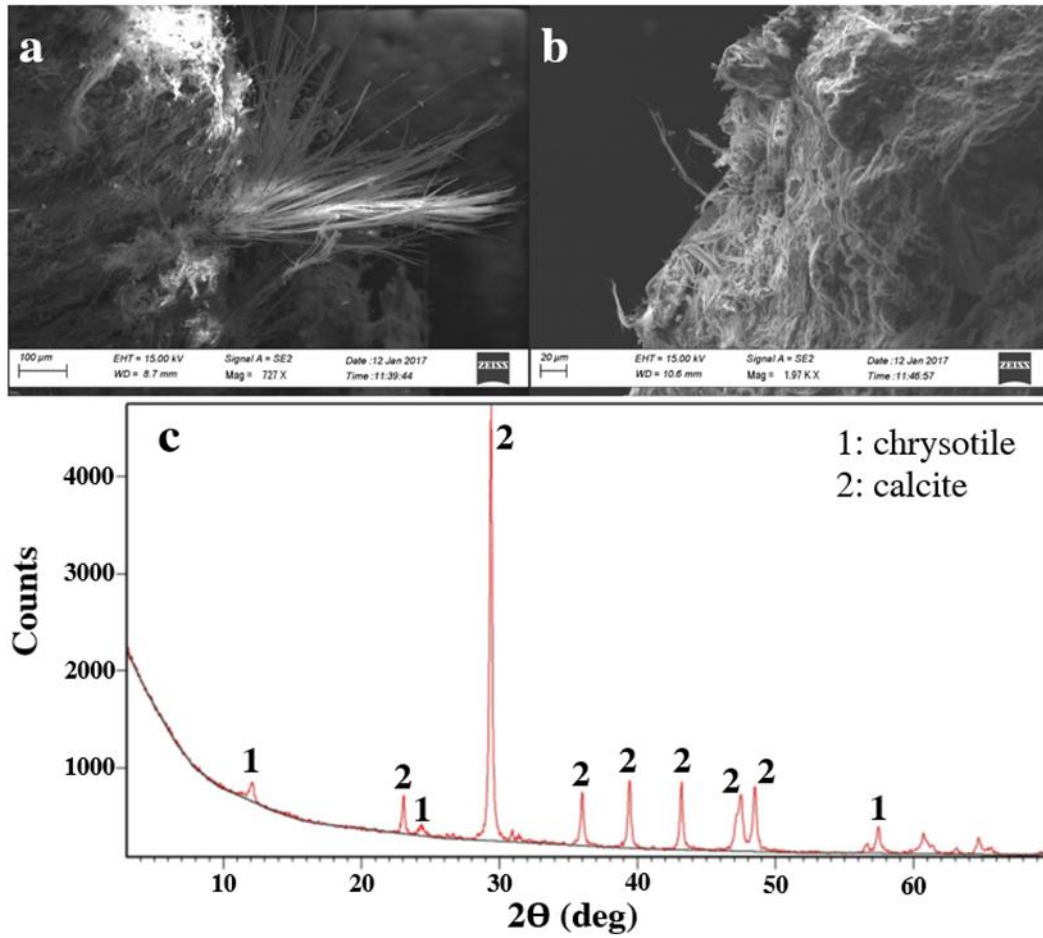


Figure 1

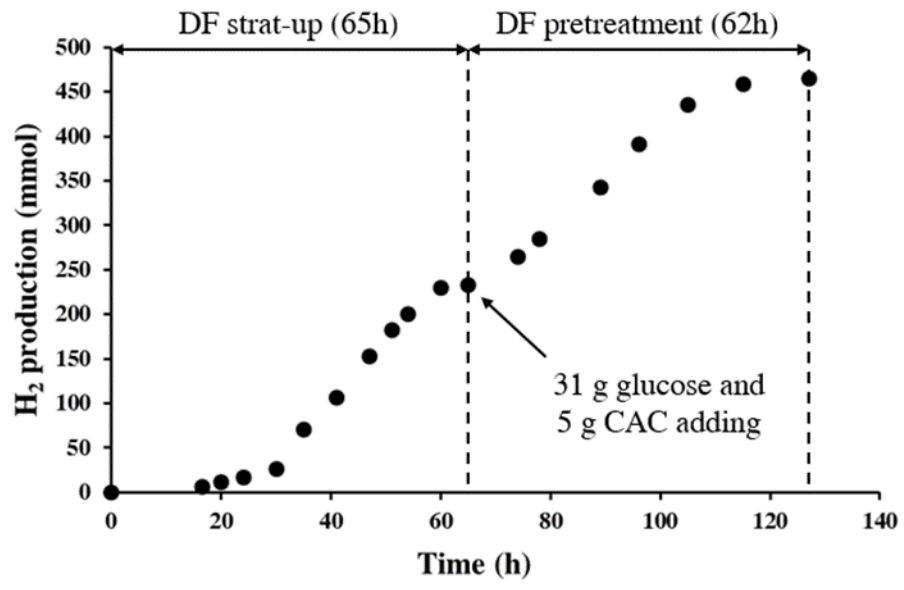


Figure 2

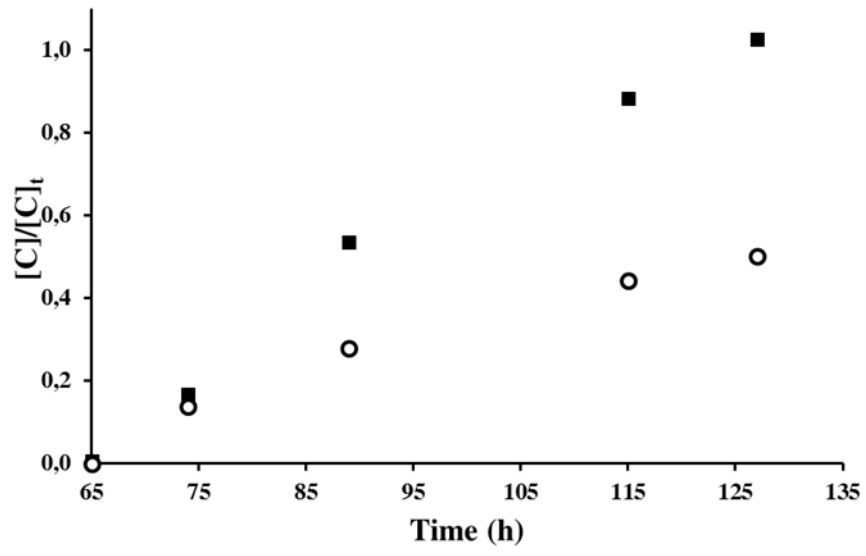


Figure 3

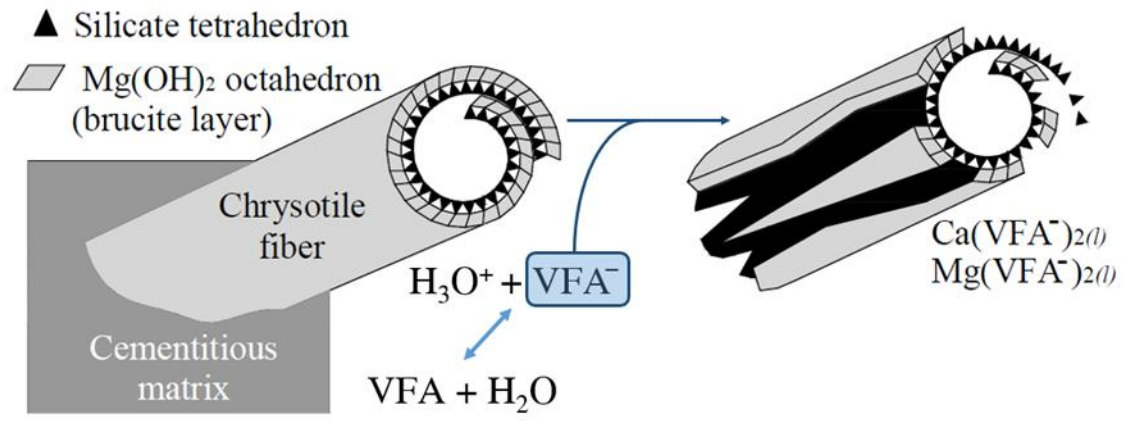


Figure 4

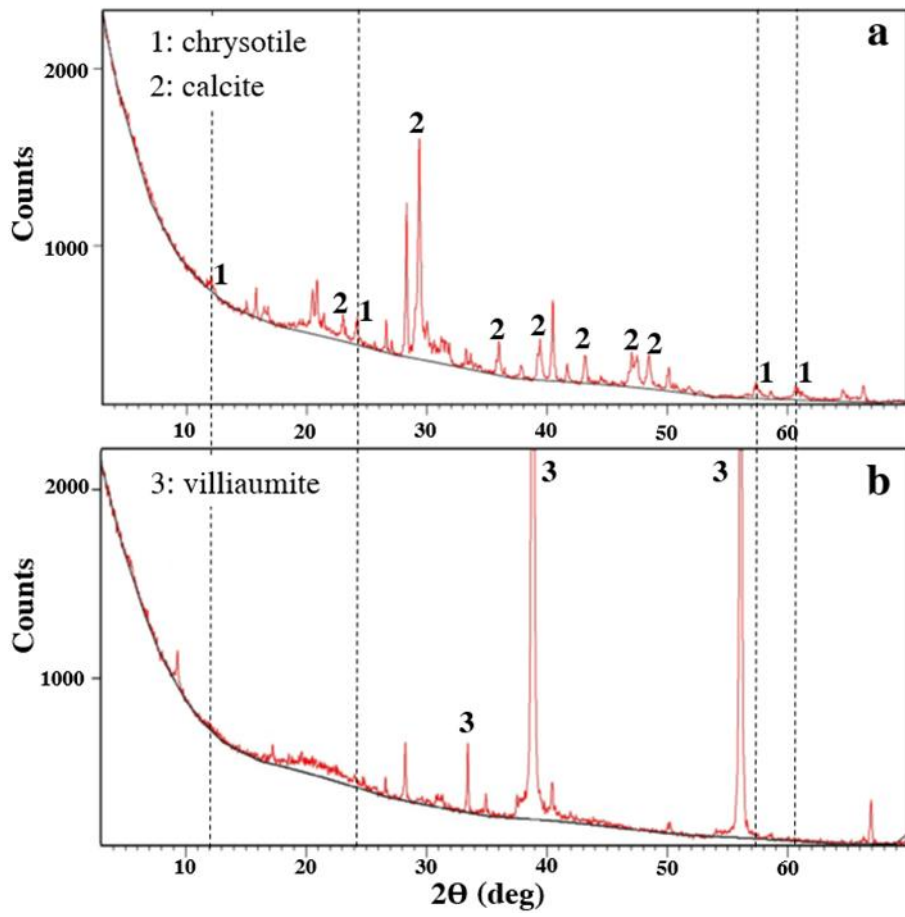


Figure 5

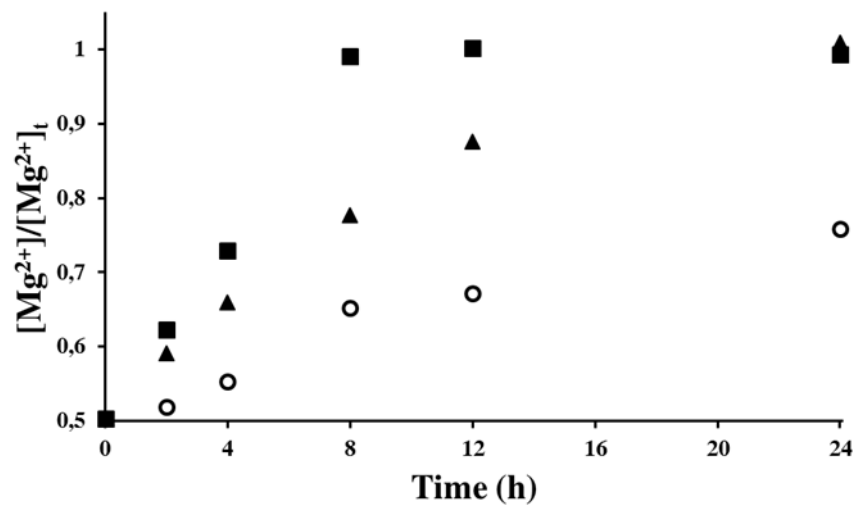


Figure 6

Figure 1. SEM and XRD analysis of the CAC used in the experimental runs.

Figure 2. Bio-hydrogen produced during the DF pretreatment. $V_{\text{sol}} = 1.0 \text{ L}$. $T = 35 \text{ }^\circ\text{C}$. $\text{pH}_0 = 7.8$.

$[\text{C}_6\text{H}_{12}\text{O}_6]_0 = 31 \text{ g L}^{-1}$. $[\text{CAC}]_{65\text{h}} = 5 \text{ g L}^{-1}$. $[\text{C}_6\text{H}_{12}\text{O}_6]_{65\text{h}} = 31 \text{ g L}^{-1}$.

Figure 3. Normalized concentrations of dissolved Ca^{2+} (■) and Mg^{2+} (○) ions during the DF pretreatment. $[\text{Ca}^{2+}]_t = 1500 \text{ ppm}$. $[\text{Mg}^{2+}]_t = 150 \text{ ppm}$. $T = 35 \text{ }^\circ\text{C}$.

Figure 4. Effect of the VFA on the CAC sample

Figure 5. XRD patterns of the samples collected at 65h after the CAC adding (a) and at the end of the DF pretreatment (b). Villiaumite (NaF) was added as internal standard with the aim of verifying the effective absence of the chrysotile peaks.

Figure 6. Normalized Mg^{2+} dissolved concentration during the hydrothermal treatment. ■: $[\text{H}_2\text{SO}_4] = 2.5 \text{ g L}^{-1}$; ▲: $[\text{H}_2\text{SO}_4] = 1.25 \text{ g L}^{-1}$; ○: $[\text{H}_2\text{SO}_4] = 0 \text{ g L}^{-1}$. $T = 100 \text{ }^\circ\text{C}$. Room pressure.

Table 1. Average element concentration of the CAC used in the experimental runs.

Table 2. VFA concentrations and pH values during the experimental run. $V_{\text{sol}} = 1.0 \text{ L}$. $T=35 \text{ }^\circ\text{C}$.

$\text{pH}_0 = 7.8$. $[\text{C}_6\text{H}_{12}\text{O}_6]_0 = 31 \text{ g}\cdot\text{L}^{-1}$. $[\text{CAC}]_{65\text{h}} = 5 \text{ g}\cdot\text{L}^{-1}$. $[\text{C}_6\text{H}_{12}\text{O}_6]_{65\text{h}} = 31 \text{ g}\cdot\text{L}^{-1}$.

SUPPORTING MATERIALS

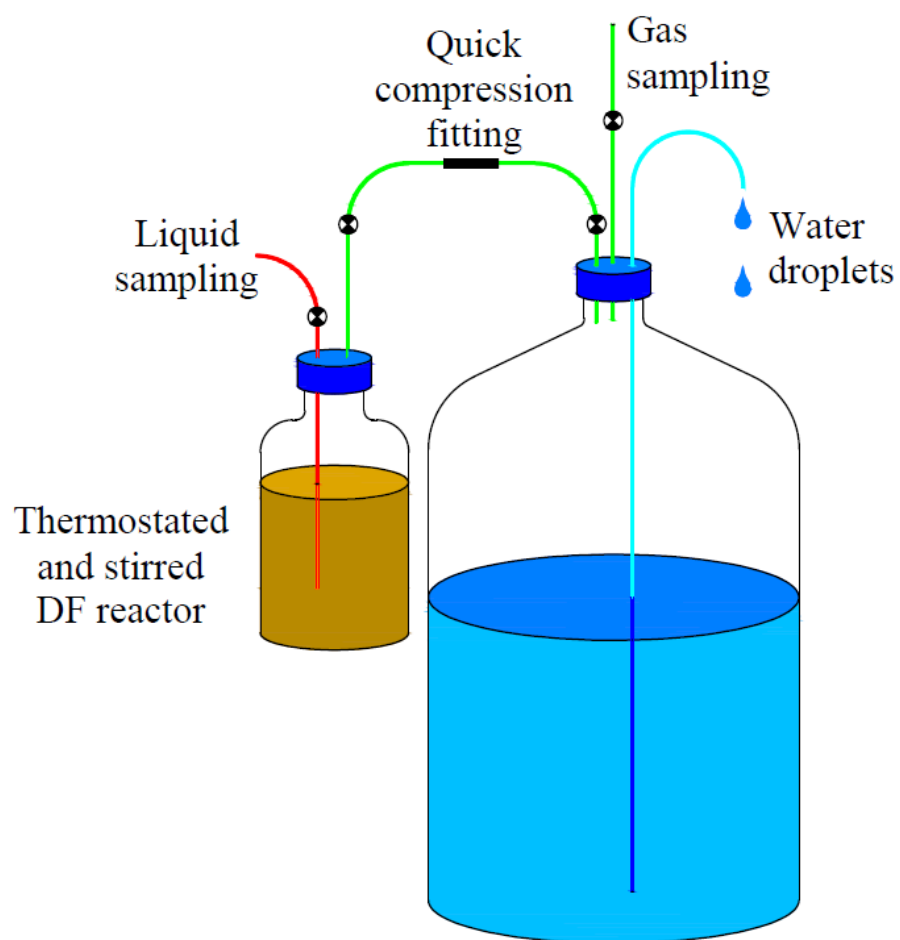


Figure 1S. DF reactor with the equipment used to measure and withdraw the gaseous samples.

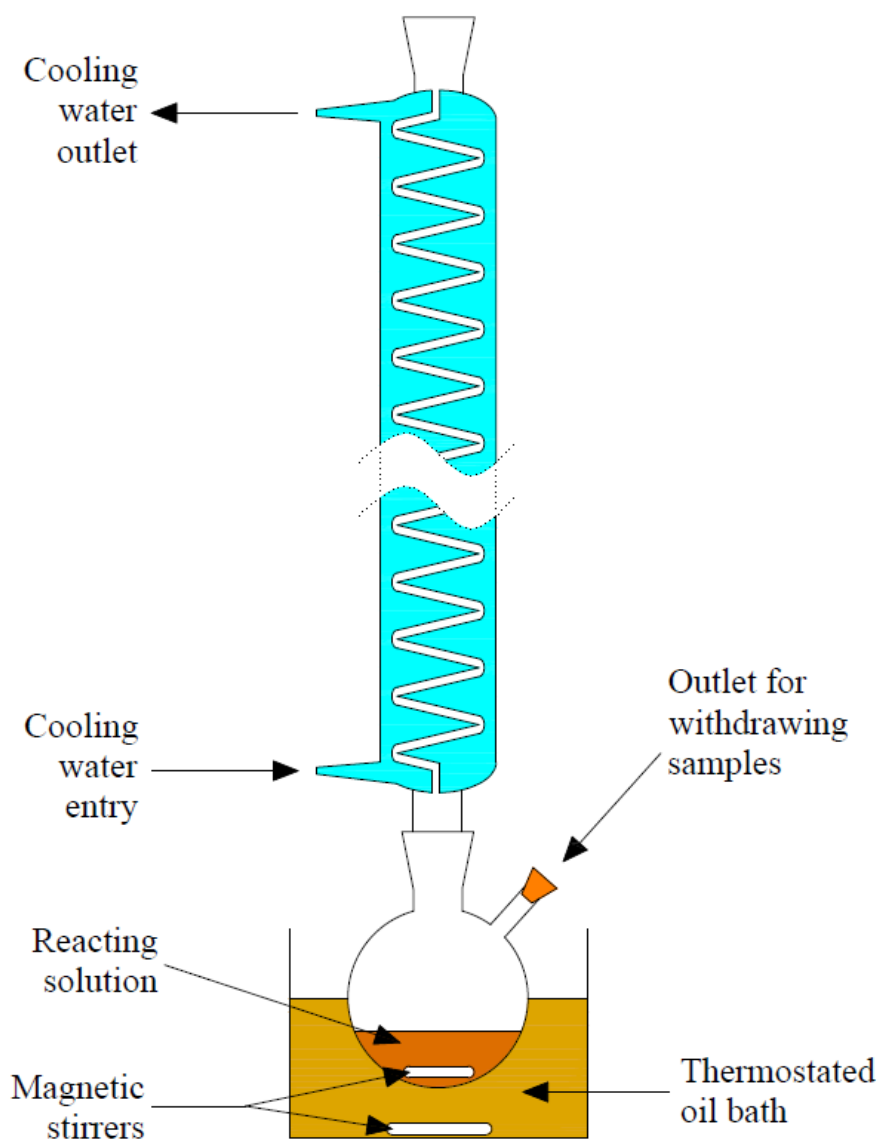


Figure 2S. Experimental apparatus used for the hydrothermal treatment.

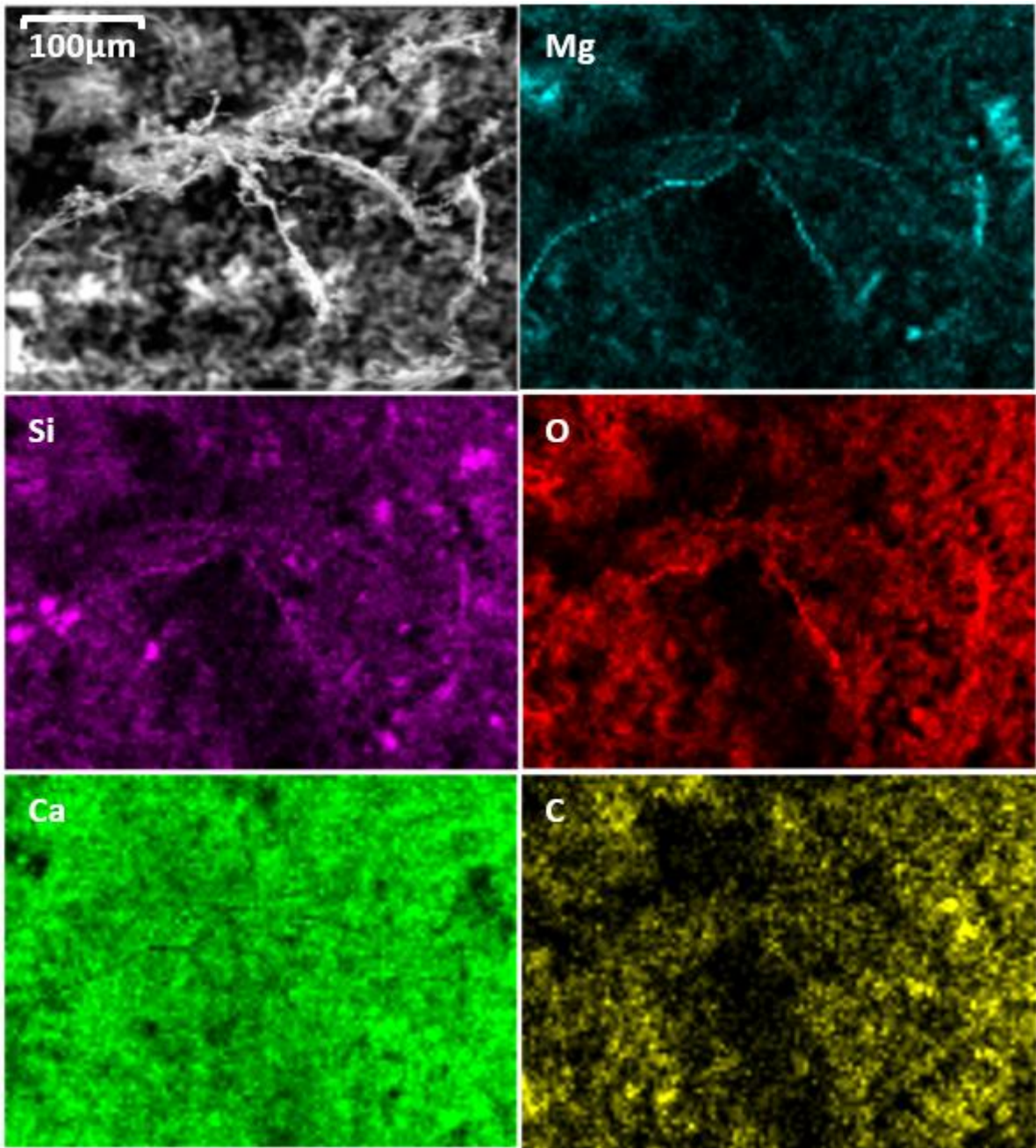


Figure 3S. CAC sample and EDX mapping of the main elements.