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.

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

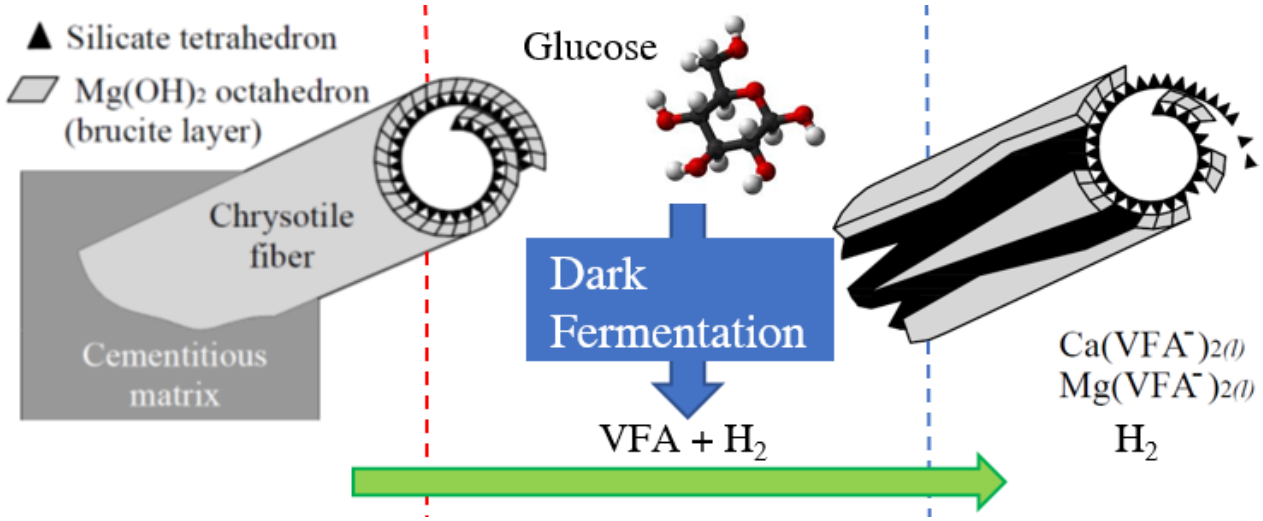
Danilo Spasiano, PhD

*Novelty Statement (maximum limit:100 words)

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.

Graphical Abstract



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 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 H_2 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 $1.0 \cdot 10^3$ € 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 ($Mg_3Si_2O_5(OH)_4$), 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 Mg^{2+} ions (1) [22-24]:

$$Mg_3Si_2O_5(OH)_4 + 3H_2SO_4 \rightarrow 3Mg^{2+} + 3SO_4^{2-} + 2SiO_2 + 5H_2O \quad (1)$$

However, CACs, which generally contain only 8-15 $\%_{w/w}$ of asbestos fibers, are characterized by the presence of calcium compounds, as calcium carbonate ($CaCO_3$), portlandite ($Ca(OH)_2$) and calcium silicates, that compete with asbestos fibers in the reaction with the acids (2) [21]:

$$CaCO_{3(S)} + H_2SO_{4(L)} \rightarrow Ca^{2+} + SO_4^{2-} + CO_2 + H_2O \quad (2)$$

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 H_2 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].

$$C_6H_{12}O_{6(L)} + \text{inoculum} \xrightarrow[\text{anaerobic conditions}]{\text{T=35 °C;}} aCO_{2(G)} + bH_{2(G)} + cVFA_{(L)} \quad (3)$$

$$Ca^{2+}_{(S)} + 2VFA_{(L)} \leftrightarrow Ca(VFA^-)_{2(L)} + 2H^+_{(L)} \quad (4)$$

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-H_2, 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

acetic, butyric, lactic, valeric, and propionic acid, which may reduce the consumption of reagents during the hydrothermal phase; iii) since agro-food wastes could be used as biodegradable compounds during the DF pretreatment, the whole process would be able to simultaneously treat two types of wastes.

However, the treatment of real CAC with the DF/hydrothermal treatment train has never been carried out. To this purpose, in this paper the adoption of the glucose DF, which would simulate a waste molasses, a by-product deriving from sugar refinery [28,29], as pretreatment of real CAC sample has been attempted for the first time.

2. Materials and methods

2.1. Materials

HPLC grade acetonitrile was purchased from Carlo Erba. Sulfuric acid (98%), nitric acid (70%), hydrochloric acid (35%), hydrogen peroxide (30%), and anhydrous glucose (99.5%) were purchased from Sigma Aldrich. All reagents and organic solvents were used as received. In all the experiments, distilled water was used as solvent.

The digestate withdrawal from the mesophilic anaerobic digestion (AD) plant of the dairy farm "Davide Colangelo" located in Capaccio (Salerno, Italy) was used for the preparation of DF inoculum. In particular, the total solids (TS), volatile solids (VS) and the pH of the AD sludge were equal to 48.15 g L^{-1}, 25.9 g L^{-1} and 7.8 respectively. The Mg^{2+} and Ca^{2+} concentration were equal to 302 ppm and 1298 ppm respectively. Moreover, no VFAs were detected.

A company handling hazardous waste provided the Eternit slate sample. In particular, the Eternit sample, was stored, cleaned, and milled with the procedure elsewhere described [21]. Finally, the sample was sieved to get a particle size below 2.0 mm, dried at 105 °C, and characterized by SEM (Figure 1a-b), EDX (Table 1) and XRD analysis (Figure 1c). In particular, the EDX mapping of the main elements of the CAC sample, reported in Figure 3S, highlights an accumulation of magnesium on the chrysotile fibers due to the presence of the brucite layer.

With regard to the calcium and magnesium concentrations in the CAC sample, they were also validated by means of a wet digestion procedure, according to the EPA method 3050 [30]. In agreement with the EDX analysis, the weight percentages of Ca and Mg evaluated with the EPA standard method were 29.9 and 3.0 respectively.

2.2. DF experimental apparatus

The DF tests were carried out with an inoculum obtained after a thermal treatment of the anaerobic digestion sludge, which inhibited the methanogenic bacteria. In particular, the digestate was heated in oven for 1 h at 105 °C as reported elsewhere [31].

In a 2.0 L air tight borosilicate glass bottle GL 45 (Shott Duran, Germany), 500 mL of inoculum were mixed with 500 mL distilled water (V_{sol} = 1.0 L). With the aim of adopting the same substrate to inoculum ratio (F/M) used in the previous investigation, 31 g L^{-1} of glucose were added to the solution [27]. Afterwards, the bottle was closed with a screw cap equipped with two sampling pipes for the withdrawal of gaseous and liquid samples. In particular, once the bottles was closed, 30 min pure nitrogen bubbling was carried out by using the liquid sample pipe as entry of the gas and the gas sample pipe as exit, with the aim of guarantee the anaerobic conditions. The DF reactor was immersed into a thermostatic bath at 35 ± 1 °C and magnetically stirred at 370 rpm. Once the production of hydrogen reached the plateau, the cap was removed and, under nitrogen atmosphere, 5.0 g L^{-1} dried CAC sample and other 31 g L^{-1} glucose were added into the solutions. Since large volumes of bio-gas were expected during the biological process, a 10 L air tight glass bottle GH 45 (Shott Duran, Germany) was used to withdrawal and measure the volume of bio-gas. At this purpose, the 10 L bottle, filled with water, was closed with a screw cap equipped with three pipes: i) the first was connected to the gas sampling tube of the biological reactor with a quick compression fitting; ii) the second was used for the gas sampling; iii) the third, which reaches the bottom of the 10 L bottle, was used to ensure the water outlet from the bottle (Figure 1S). In particular, the volume of biogas produced during the test was measured by disconnecting the quick compression

fitting after closing the upstream and downstream valves. Afterwards, the 10 L and 2 L bottles were connected to a eudiometer to measure the volume of bio-gas under pressure. The whole produced biogas was considered as the sum of the volumes measured with the eudiometer and the volume of water necessary to refill the 10 L bottle.

2.3. Hydrothermal experimental apparatus

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

2.4. Analytical methods

Both Ca^{2+} and Mg^{2+} dissolved ion concentrations were quantified by atomic absorption spectrometry using a Varian Model 55B SpectrAA (F-AAS) equipped with a flame (acetylene/air) and a deuterium lamp for background correction.

Biogas composition was evaluated with a Varian Star 3400 gas chromatograph equipped with ShinCarbon ST 80/100 column and a thermal conductivity detector. Argon was used as carrier gas with 1.4 bar front and rear end pressure.

The concentrations of the organic acids were measured with a high pressure liquid chromatography. Specifically, a Dionex LC 25 Chromatography Oven equipped with a polymer-based cation-exchanger column (Metrohm Metrosep Organic Acids - 250/7.8) and a Dionex AD25 Absorbance Detector were combined with a gradient pump (Dionex GP 50), eluting the samples with sulphuric acid 0.5 mM at the flow rate of 0.7 mL min^{-1}.

SEM images and EDX analysis of the solid samples were carried out with an electron microscope FESEM-EDX Carl Zeiss Sigma 300 VP. In particular, the samples were fixed on aluminum stubs and then sputtered with gold with a Sputter Quorum Q150.

The samples were analyzed for their mineralogy using a PANalytical X'Pert Pro diffractometer, at 40 kV and 40 mA, using Cu Kα radiation, with divergence slit of 0.5, spinner revolution 1 mm s^{-1}. The apparatus was equipped with a solid-state detector (X'Celerator) covering an angle of 2.1° and integrates the diffracted intensity as it scans. The powders were scanned in the range 3–70° 2θ.

In particular, the SEM, EDX, and XRD characterization of the solids suspended into the DF solution and the hydrothermal effluents were carried out on the solid phase deriving from the centrifugation (4500 rpm at 4 °C) of 50 ml samples. Before its characterization, the solid phase, having a muddy appearance, was lyophilized with a single chamber lyophilizer (Martin Christ Alpha 1-4 LSCplus) and then ground in an agate planetary ball mill.

Total solids and volatile solids and COD were measured according to APHA standard methods [32]. The pH of the solution was monitored with a Hanna Instruments HI 98190 pH/ORP pH-meter.

3. Results and discussion

3.1 DF pretreatment

The start-up of the DF pretreatment consisted in the addition of 31 g of glucose in the bioreactor (V_{sol} = 1.0 L) in absence of the CAC sample. During this phase, lasting 65 h, the microorganisms degraded the glucose producing VFAs, which lowered the pH of the solution to 5.45, and 233.8 mmol of bio-hydrogen. Afterwards, when the H_2 production reached the plateau, 5 g of CAC were added to the solution together with other 31 g of glucose. As a result, the already activated fermentative bacteria immediately started to degrade the substrate leading to an almost constant H_2 production, which terminated after 62 h (t_f =127 h), reaching a bio-H_2 production of 465.4 mmol (Figure 2). During the process, as reported in table 1, the VFA production raised and the pH of the solution decreased.

As a result, after the CAC addition, it was observed the dissolution of the cement matrix and of the brucite layer ($Mg(OH)_2$) 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 ($[Ca^{2+}]_{65h}$ = 649 ppm; $[Mg^{2+}]_{65h}$ = 155 ppm) and were normalized with respect to the theoretical concentrations ($[Ca^{2+}]_t$ = 1500 ppm. $[Mg^{2+}]_t$ = 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 (pH > 6) and the solvent production (pH < 4.5) [35,36].

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 vitelline*, 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].

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

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 H_2SO_4 were added to the solution, a ratio $[H_2SO_4]/[CAC]$ 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 H_2SO_4 has been saved.

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

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-H_2, 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 $[H_2SO_4]$/[CAC] ratio equal to 0.25, which is half of that previously reported.

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

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Table

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 (h)	Formic Acid (ppm)	Acetic Acid (ppm)	Butyric Acid (ppm)	Lactic Acid (ppm)	pH
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
Click here to download Figure: figures.docx

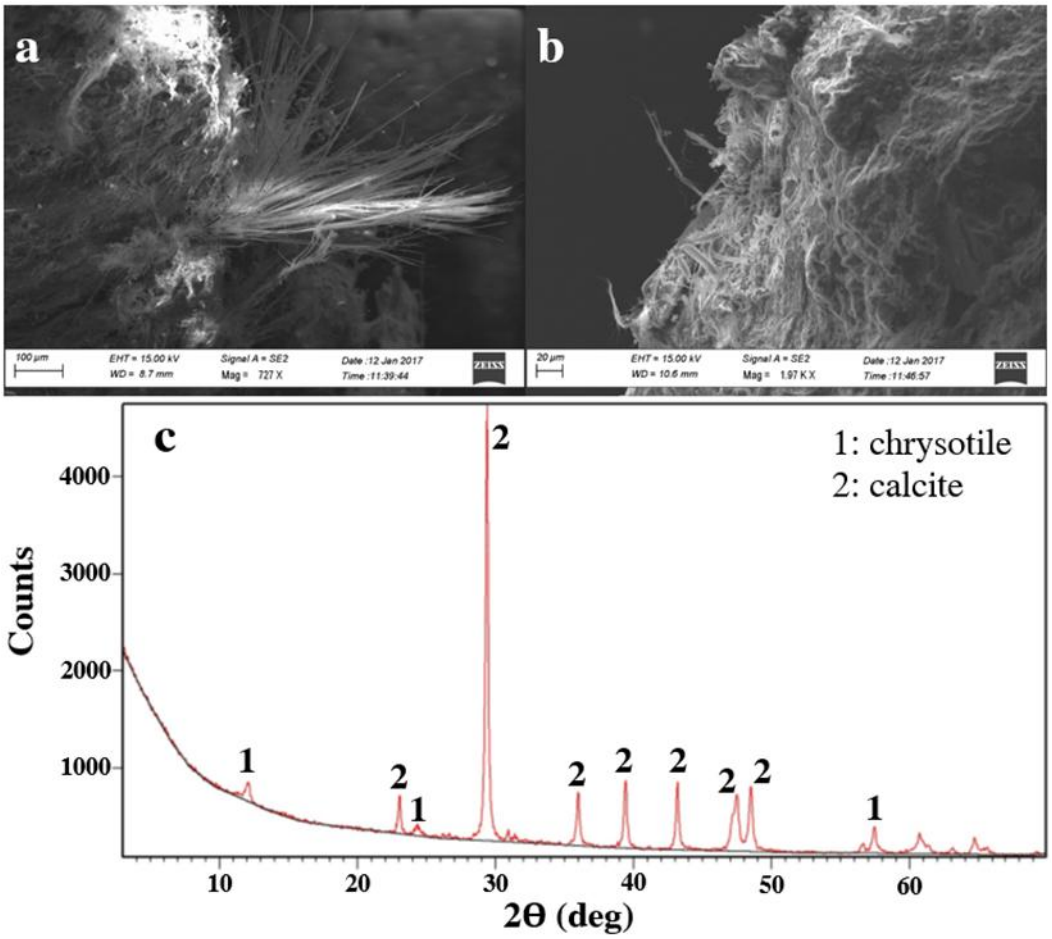

Figure 1

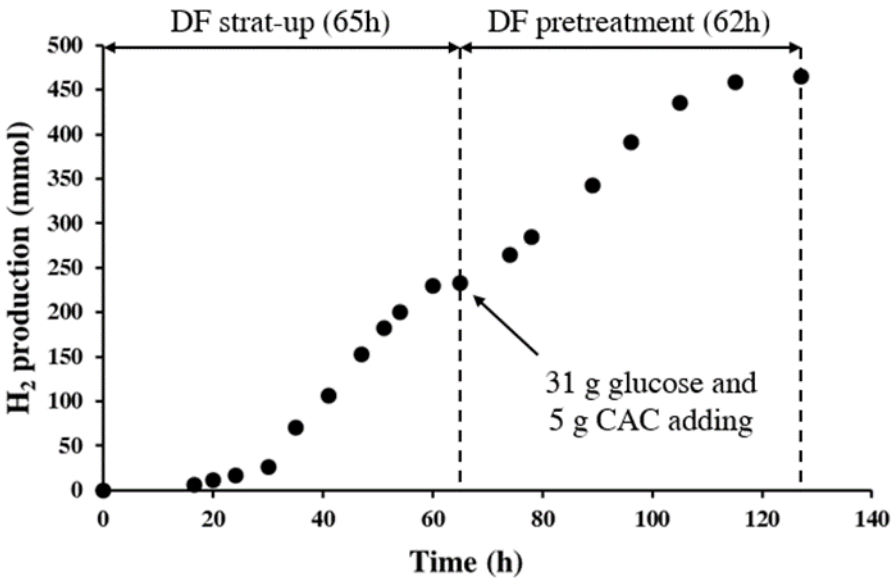
DF strat-up (65h)
DF pretreatment (62h)
H_2 production (mmol)
Time (h)
31 g glucose and
5 g CAC adding
0
50
100
150
200
250
300
350
400
450
500
0
20
40
60
80
100
120
140

Figure 2

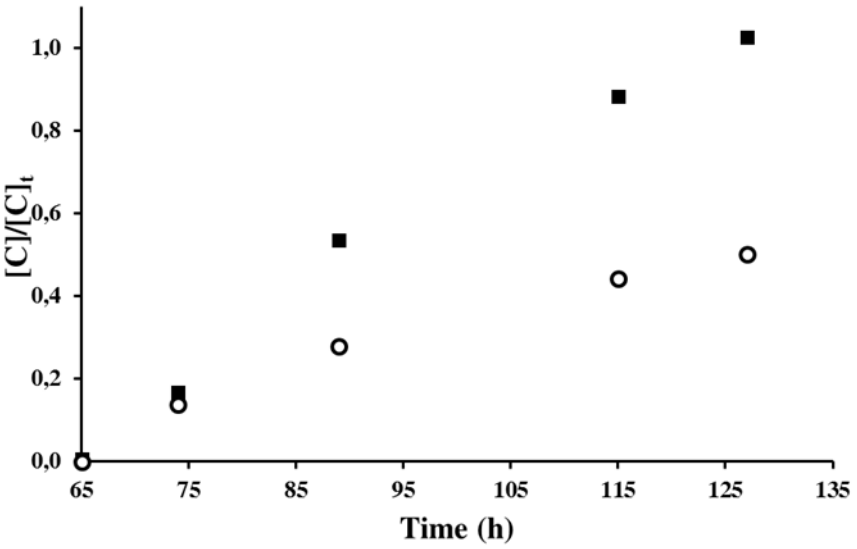

Figure 3

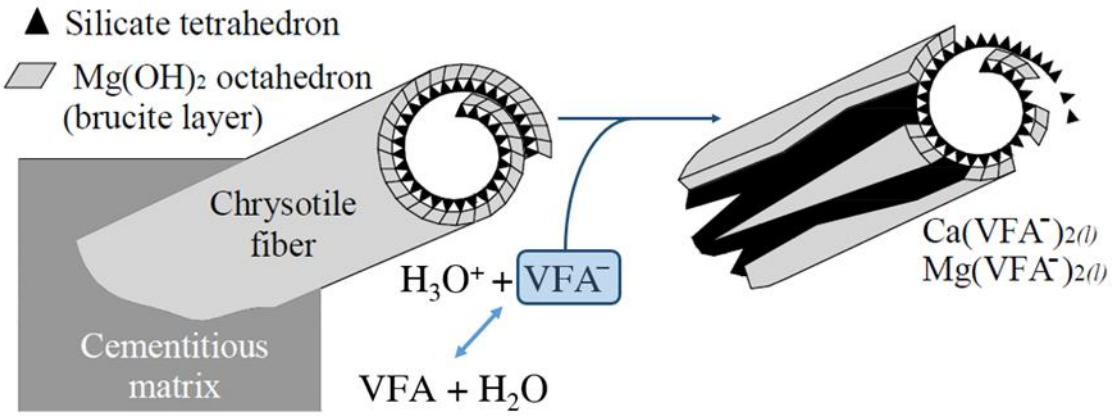
Silicate tetrahedron
Mg(OH)2 octahedron
(brucite layer)
Chrysotile
fiber
Cementitious
matrix
H3O+ + VFA−
VFA + H2O
Ca(VFA−)2(l)
Mg(VFA−)2(l)

Figure 4

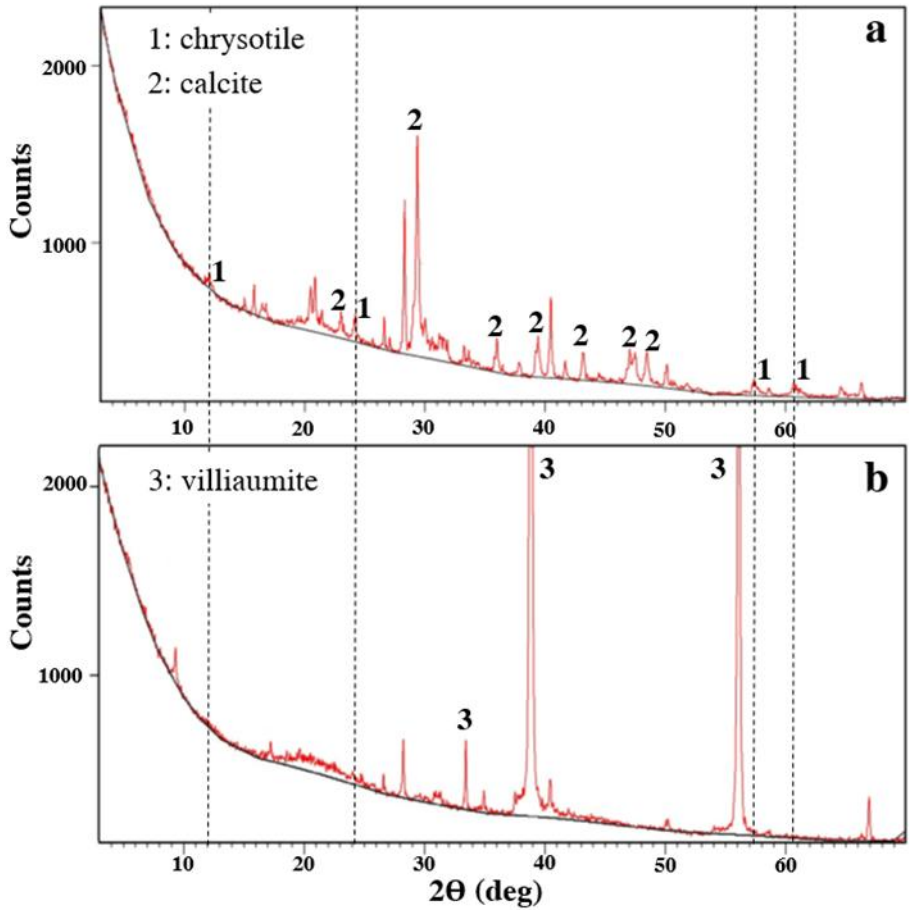
1: chrysotile
2: calcite
a
Counts
2000
1000
10
20
30
40
50
60
3: villiaumite
b
2θ (deg)

Figure 5

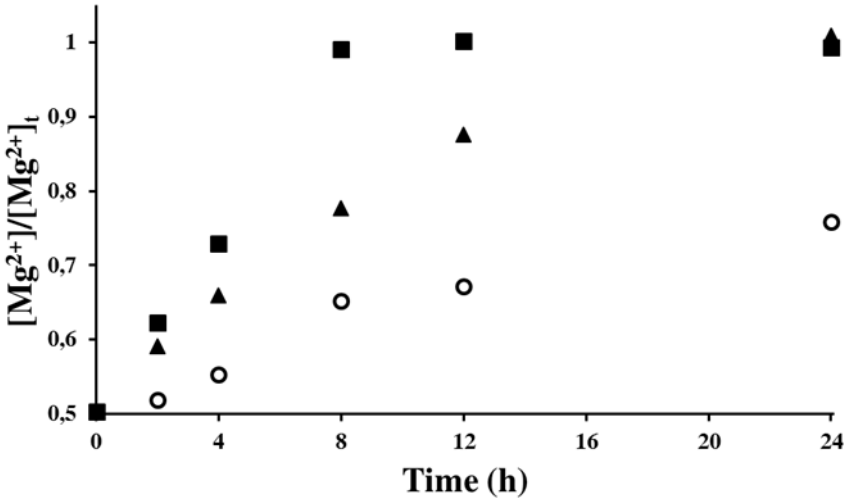

Figure 6

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

Figure 2. Bio-hydrogen produced during the DF pretreatment. V_{sol} = 1.0 L. T = 35 °C. pH_0 = 7.8. $[C_6H_{12}O_6]_0$ = 31 g L^{-1}. $[CAC]_{65h}$ = 5 g L^{-1}. $[C_6H_{12}O_6]_{65h}$ = 31 g L^{-1}.

Figure 3. Normalized concentrations of dissolved Ca^{2+} (■) and Mg^{2+} (○) ions during the DF pretreatment. $[Ca^{2+}]_t$ = 1500 ppm. $[Mg^{2+}]_t$ = 150 ppm. T = 35 °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. ■: $[H_2SO_4]$ = 2.5 g L^{-1}; ▲: $[H_2SO_4]$ = 1.25 g L^{-1}; ○: $[H_2SO_4]$ = 0 g L^{-1}. T = 100 °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_{sol} = 1.0 L. T=35 °C. pH_0 = 7.8. $[C_6H_{12}O_6]_0$ = 31 g·L^{-1}. $[CAC]_{65h}$ = 5 g·L^{-1}. $[C_6H_{12}O_6]_{65h}$ = 31 g·L^{-1}.

SUPPORTING MATERIALS

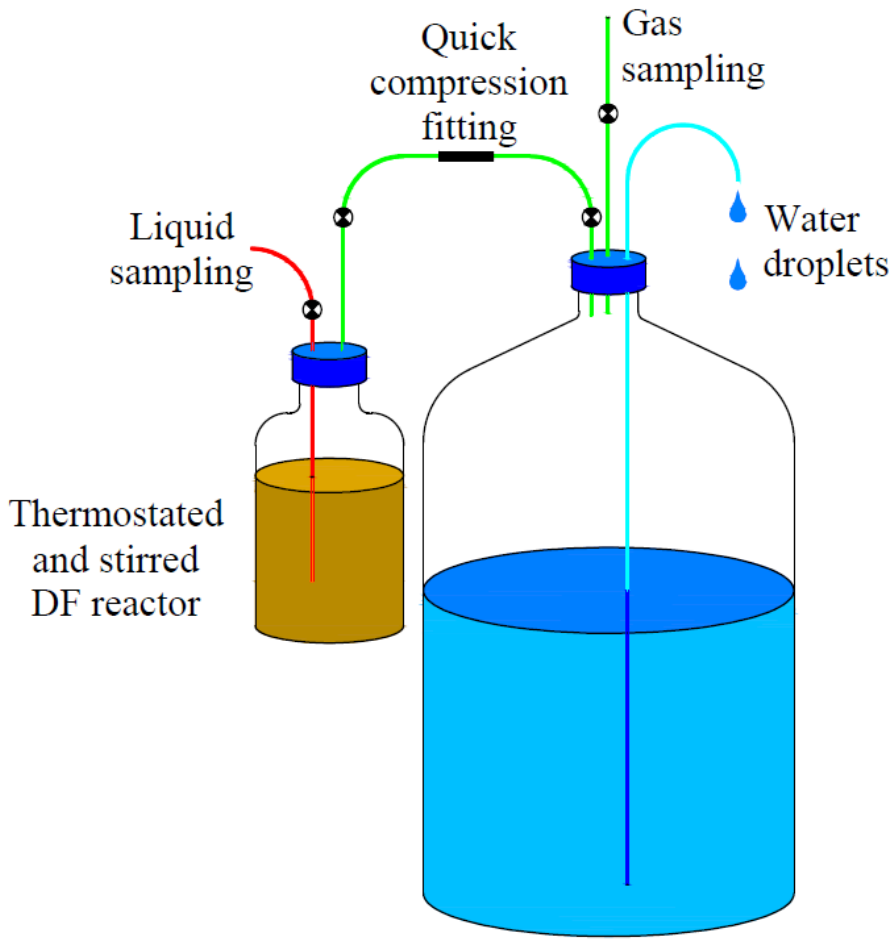

Figure 1S. DF reactor with the equipment used to measure and withdraw the gaseous samples.

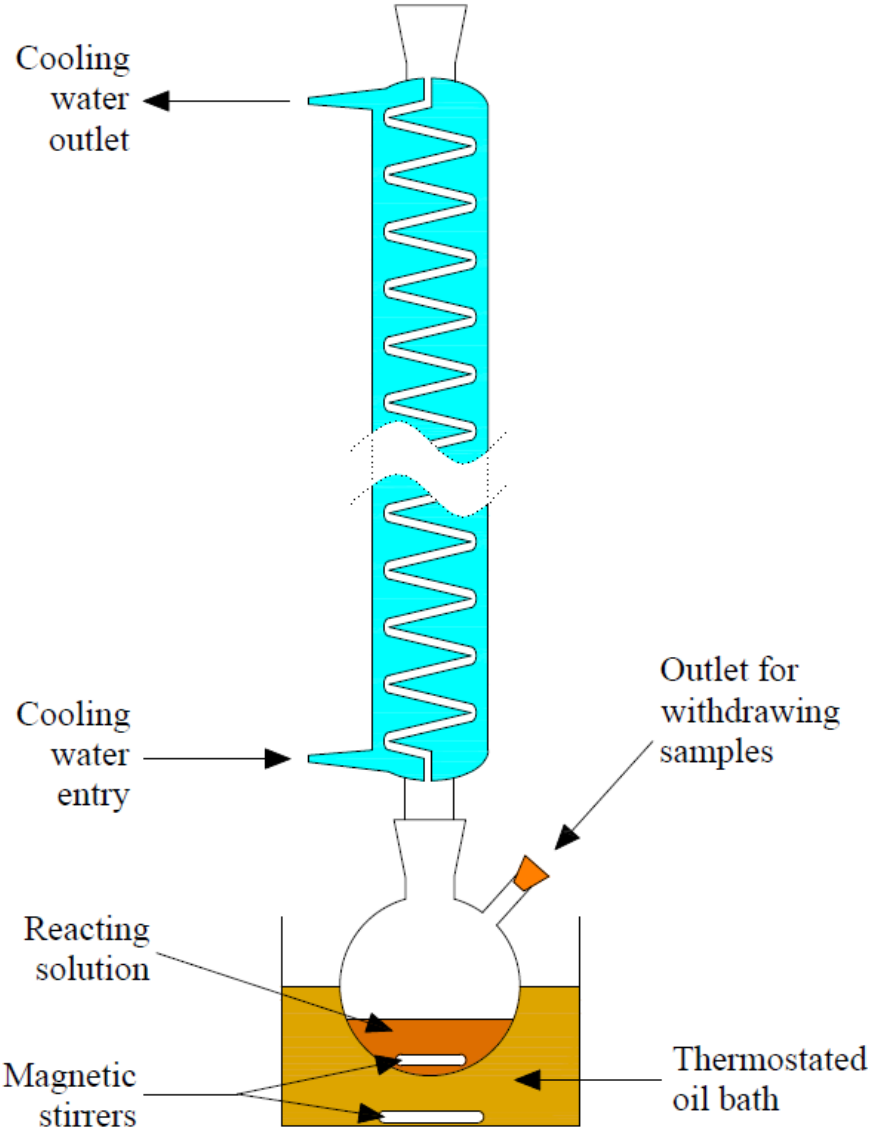

Figure 2S. Experimental apparatus used for the hydrothermal treatment.

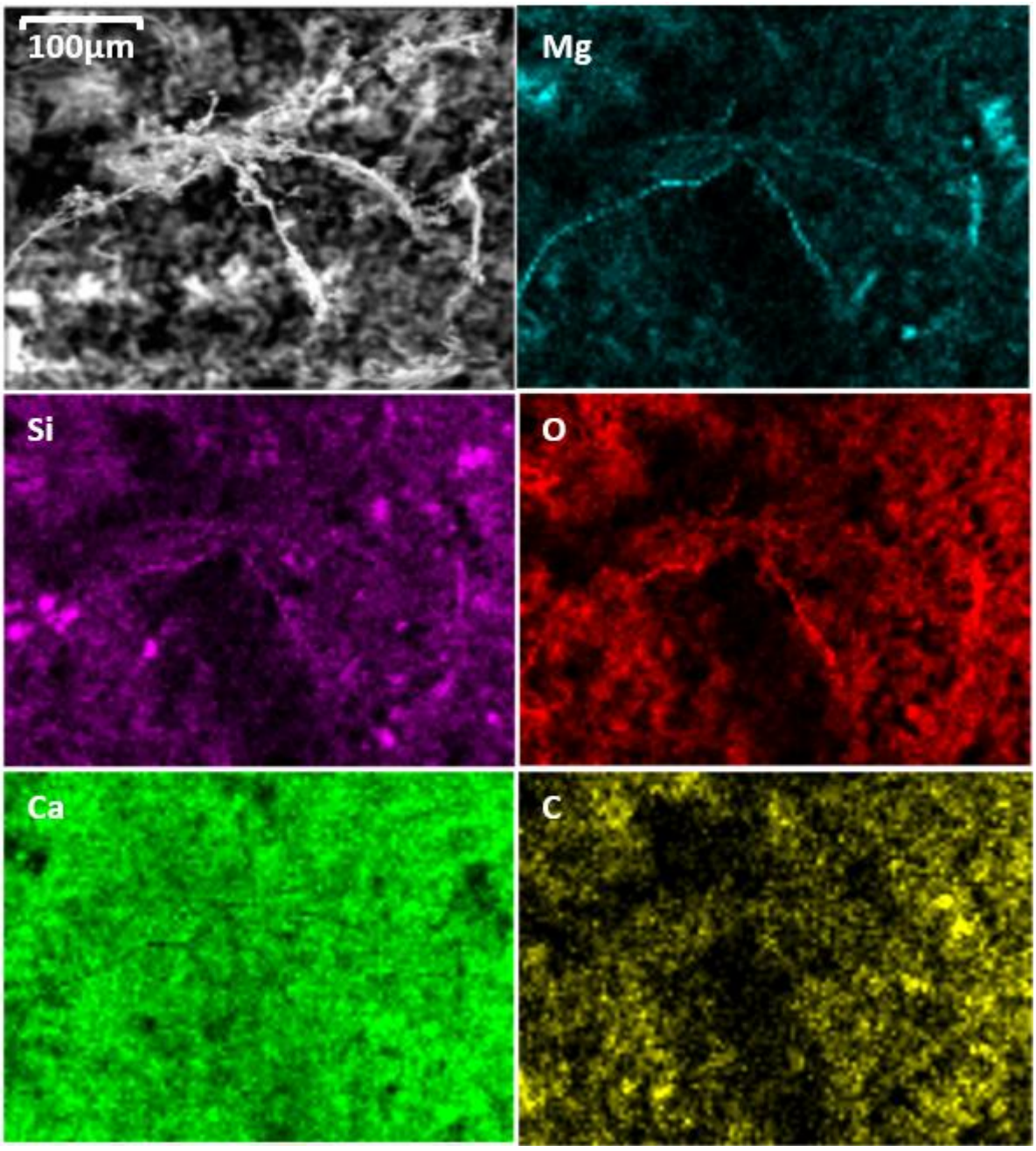

Figure 3S. CAC sample and EDX mapping of the main elements.