Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 97 (2016) 515 – 522

Energy Procedia

European Geosciences Union General Assembly 2016, EGU
Division Energy, Resources & Environment, ERE

Self-Sustained Combustion Synthesis and Asbestos-Bearing Waste: Scaling Up From Laboratory Towards Pre-Industrial Size Plant

Laura Gaggero[a], Valentina Caratto[b] *, Maurizio Ferretti[b]

[a]*Department of Earth, Environment and Life Sciences - DISTAV, University of Genoa, Corso Europa 26, I-16132 Genoa*
[b]*Department of Chemistry and Industrial Chemistry – DCCI, University of Genoa, Via Dodecaneso 31, I-16146 Genoa*

Abstract

An apparatus and a technique were developed for triggering the breakdown reaction of chrysotile by means of a combustion synthesis well known as Self-propagating High temperature Synthesis or SHS. The experiments were carried out varying different Asbestos-Containing Waste (ACW). The reactions were carried in a continuous-feeding configuration, indispensable for the development and fine-tuning of the process parameters towards industrial scale up. Experiments demonstrated to be effective in destructing the fibrous habit of chrysotile. The SHS process in comparison with conventional thermal treatments, due to fast reaction time and low activation energy, positively reflects into time and costs of the process.

Peer-review under responsibility of the organizing committee of the General Assembly of the European Geosciences Union (EGU)

Keywords: asbestos waste, fibre cement, industrial waste, inertisation, chrysotile, olivine, fibres

1. Introduction

The asbestos minerals have been used for a number of applications due to their excellent physical properties that include non-flammability, high tensile strength, heat and electrical insulation, resistance to chemical and biological agents [1-2]. Following the dismissal of asbestos in industrial and civil uses, increasing amounts of fibre-bearing

* Corresponding author. Tel.: +39 010 3538737; fax: +39 010 3538733
E-mail address: caratto@chimica.unige.it

Peer-review under responsibility of the organizing committee of the General Assembly of the European Geosciences Union (EGU)
doi:10.1016/j.egypro.2016.10.064

wastes represent a first rank alert. This type of waste will further increase as the European Parliament, in March 2013, approved a resolution (2012/2065INI) adopting a common strategy for the total elimination of the asbestos still remaining in European buildings, machinery, tubing, trains and ships by 2028 [3].

Technical literature presents several treatment possibilities: the patented ones deal with the utilization and neutralization of asbestos and the asbestos products. The methods encompass both basic research and the applications of chemical [4-6] or thermal treatments of the waste [7-9]. We developed an apparatus and a technique for obtaining the breakdown reaction of chrysotile by means of an alumino-thermic reaction and of the process of combustion synthesis or Self-propagating High-temperature Synthesis. This approach yielded positive results and allowed the development of an efficient method for inerting natural asbestos fibers and man–made products carrying fibers, at the scale of some grams. Based on the preliminary experiments, a patent was deposited [10].

The Self-propagating High-temperature Synthesis [11-12] takes advantage from the enthalpy variation of an alumino-thermic reaction, i.e. an oxy-reduction reaction between a metallic oxide and aluminum or another reducing reagent. The reaction is characterized by strong exothermicity, being even self-sustaining. Once triggered by an external heat source for a few seconds, the reaction proceeds across the volume of reagents as a combustion wave, without the need of further energy input from outside.

This allows to obtain some advantages of the plasma combustion, such as the high density of thermal energy and the high temperature (1600°C) but with significantly lower costs due to the short time of heat induction.

The final products are granular silicates and oxides, (e.g. granular forsterite), reusable as abrasive, refractory or ceramic second raw material, or, at worst as aggregates.

A study for the inertisation of fibrous waste through the SHS technique has been performed by Porcu et al. [12]; in particular they used glass fibers, sepiolite and friable asbestos in a laboratory batch process with a few grams of processing capacity. The ignition of the reaction occurred through a white-hot coil of W.

The aim of this work was to test I) a continuously fed process II) triggered with an oxyacetylene flame that III) can handle hundreds of grams of asbestos -containing waste, as a first part of an industrial scale up.

2. Experimental

2.1. The experimental apparatus

Based on the state of the art reached in the development of the patented prototype [11] a new prototype was designed aiming at processing continuous batches with a treatment capacity up to 500 g.

It is composed of (Fig. 1):

A) an automated horizontal feeder made of two serial pushers with mechanical screw. A dedicated software interface allowed to test the optimal feed rate to match the reaction speed;

B) an horizontal oven for pre-heating of the waste, kept at a T 400-600°C depending on the type of waste and on the appropriate feed rate;

C) a reaction chamber with two large windows for inspection and for recording the process. The reaction occurs under Ar flow (Siad 99.998%); an oxy-acetylene torch triggers the reaction at the head of the pre-heated ACW batch

D) an underlying tank, filled with water where the burnt sample is dropped and cooled after reaction. The tank also inhibits the dispersion of dusts from the sample.

E) by means of a high energy air extractor, the prototype, installed inside a Clean Room, operates under depressed atmosphere as mandatory safety prescriptions.

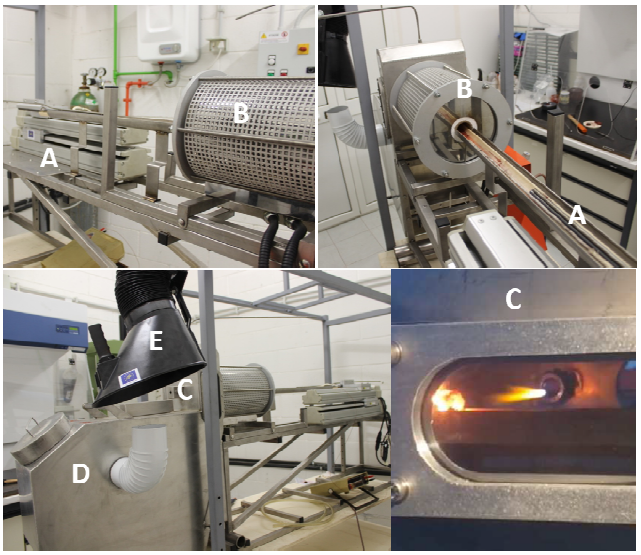

Fig.1 Different views of the prototype. The letters correspond to the different parts described in the text. Bottom right panel shows the oxy-acetylene torch triggering the reaction.

2.2 Materials

In this work we experimented the use of Self-propagating High-temperature Synthesis (SHS), exploiting the highly exothermic and fast self–propagating high-temperature reaction:

$$Fe_2O_3 + 4\ Mg \rightarrow 4\ MgO + 3\ Fe \qquad \Delta H_r = -\ 983{,}2\ kJ/mol$$

The reactants used were Fe_2O_3 (La Betoncolor s.a.s, 96% purity) and Magnesium powder (Chemetall Italia S.r.l. 99% purity, grain size 63 – 100 µm).

In the previous experiments [13] we observed that natural chrysotile, mixed in appropriate amounts with these reagents, was completely converted into forsterite-rich olivine by a highly exothermic reaction in spite of heat absorption during the transformation of chrysotile. Different mixtures of Fe_2O_3 + Mg were tested to establish the minimum amount needed to start the reaction.

The new experiments addressed the reaction with different Asbestos-Containing Waste (ACW) as friable asbestos and fibre cement and different amounts of reagents (from 50 to 25 weight % for friable asbestos and from 50 to 40 weight % for fibre cement).

Before the reaction, the samples underwent pre-heating at a T of 400-450°C for a few minutes. During this step the whole sample is equilibrated towards the T of triggering in order to properly start the combustion; this helps to reduce the dispersion of the reaction heat.

2.3. Characterization of materials

Before and after the SHS reaction all samples were characterized by SEM-EDS (Vega 3 LMU Tescan). A Scanning Electron Microscope Tescan Vega 3 LM equipped with a Apollo X detector and Microanalysis TEAM EDS System acquired images and mineral compositions. Microphotographs were carried out on gold–sputter coated 3D samples under high vacuum conditions with backscattered and secondary detectors. Semiquantitative electron microprobe analyses of phases were obtained under high-vacuum conditions by use of natural standards. Operative conditions were: voltage 15 to 20 eV.

X-ray diffraction patterns of samples were performed on a Philips PW 1140 diffractometer using the Bragg–Brentano geometry, with Cu Kα radiation (λ = 0.15406 nm), input 40 KV; electric current intensity: 20 mA; start

angle 3°; total scanning: 80°).

3. Results and discussion

Figure 2 shows the SEM characterization of friable asbestos (A) and fibre cement (B) used for all combustion tests; both waste have a fibrous habit.

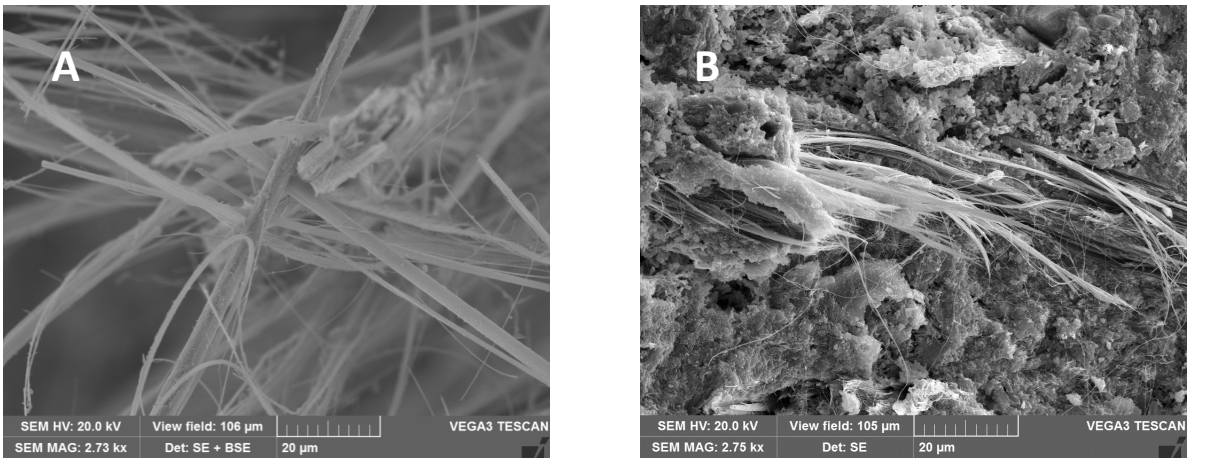

Fig. 2. SEM microphotographs of friable asbestos (A) and fibre cement (B) waste types before SHS reaction.

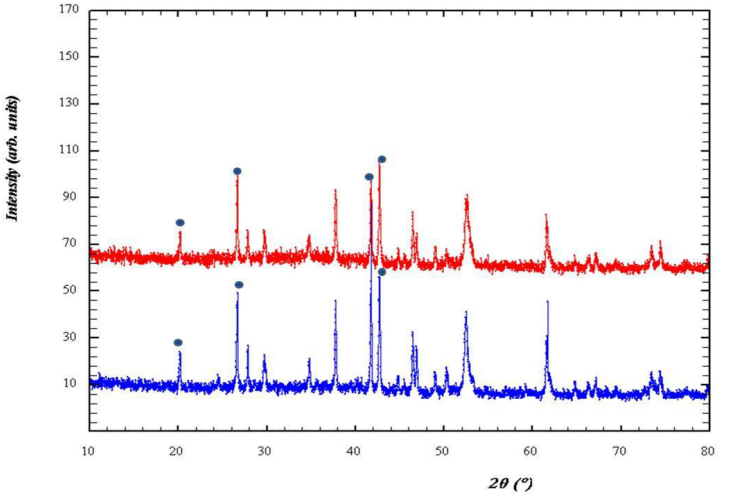

Fig. 3. Intensity pattern of the mineral aggregate composing the friable asbestos fibers (red) and fibre cement (blue). The evidenced peaks correspond to chrysotile. Others peaks represent the calcite and quartz matrix.

The friable fibrous waste was mixed with appropriate amount of Fe_2O_3 and Mg; the powdered sample was then inserted in a mould and pressed to 200 bars to obtain compact cylinders. Then the samples were placed in the prototype oven.

Several tests were carried out from a composition of 50 weight % reagents downward, increasing the % of treated waste. Also the minimum T (from 25 to 500°C) needed to gain a pre-heating able to trigger a SHS reaction was

systematically tested. The reaction with pre-heating T lower than 400°C could not be triggered by the oxy-acetylene flame.

The feed rate of the plant to the combustion chamber corresponds to 1 mm/sec, and was kept constant as this is the speed of propagation of the SHS reaction measured in the fibrous matrix [13]. Taking into account the length of the reaction chamber the pre-heating time resulted of 300 seconds. Finally, the whole of the tests defined the optimal parameters for minimum preheating T sufficient to start the reaction (Table 1).

Table 1. Experimental parameters for SHS treatment of friable asbestos.

Sample	Waste type	wt % waste	Pre-heating T (°C)	Reaction result
FIBERS-1	Friable asbestos	50	400	Achieved
FIBERS-2	Friable asbestos	60	400	Achieved
FIBERS-3	Friable asbestos	70	450	Achieved
FIBERS-4	Friable asbestos	75	450	Partially achieved

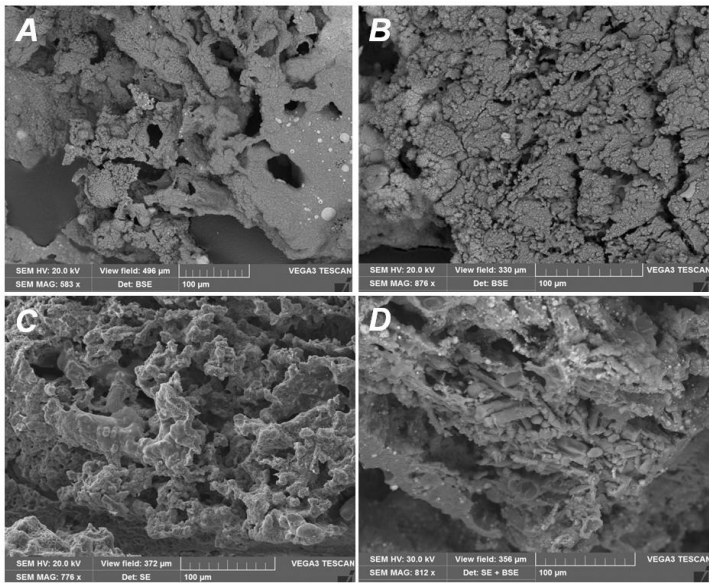

Fig. 4. SEM microphotographs after the SHS reaction: FIBERS-1 (A), FIBERS-2 (B), FIBERS-3 (C) and FIBERS-4 (D), corresponding to the wt% waste of Tab.1.

After SHS reaction, the samples FIBERS-1, FIBERS-2 and FIBERS-3 (Fig. 4) show a granular morphology and fibers are no more present. In sample FIBERS-4 some elongated grains are present (centre of the photo). However the ratio L/d < 3 demonstrates the loss of the fibrous habit and the development of sturdy prisms, that cannot be defined fibers anymore. Extensive analysis of the microtextures evidenced that the SHS reaction was pervasive.

The XRPD analysis (Fig. 5) confirms the SEM imaging results. Samples FIBERS-1, FIBERS-2, FIBERS-3 contain olivine instead of pristine chrysotile.

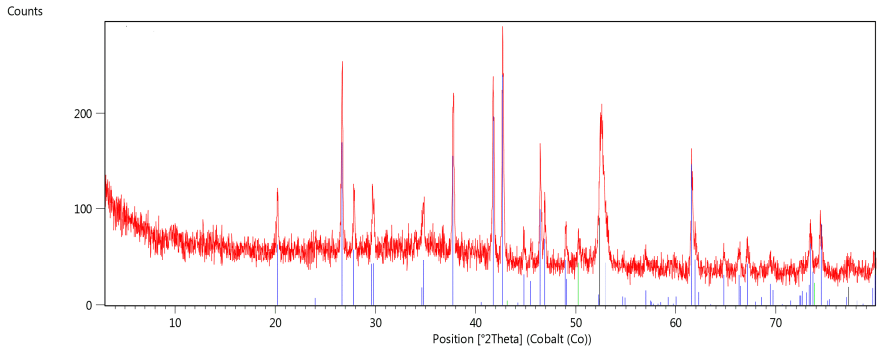

Fig. 5. Intensity pattern of the mineral aggregate composing sample FIBERS-3. Interpretation of the phases in the mineral mixture: olivine (blue), MgO (green), Fe (black)

The same tests were carried out also for the fibre cement waste. The samples were ground with a Retsch Mill BB50 with a 0.8 mm gap width and 450 rpm speed, then were mixed with reagents in different amounts. The grinding of material resulted to be necessary to attain a homogeneous mixture without asbestos-rich or reagent – poor volumes that could cause the reaction off. The powders were then addressed to the continuous prototype as was for the friable waste.

Finally, the whole of the tests defined the optimal parameters for minimum preheating T sufficient to start the reaction with fibre cement waste (Table 2).

Table 2. Experimental parameters for SHS treatment of fibre cement waste.

Sample	Waste type	wt % waste	Pre-heating T (°C)	Reaction result
FIBERS-6	Fibre cement	55	400	Achieved
FIBERS-6	Fibre cement	55	400	Achieved
FIBERS-7	Fibre cement	60	500	Partially achieved

After SHS reaction, the samples FIBERS-5 and FIBERS-6 (Fig. 6) have no longer a fibrous habit, while FIBERS-7 sample still shows unreacted asbestos. The XRPD analysis (Fig. 7) confirms that olivine was obtained as a product. As a conclusion, the optimum conditions for the inertisation of asbestos cement are obtained at 55 weight % waste.

In spite of the high amount of reagents needed to attain the complete inertisation compared to friable asbestos, the result is highly positive, as for the first time the SHS technique was successfully applied to fibre cement, and confirms as a new effective treatment.

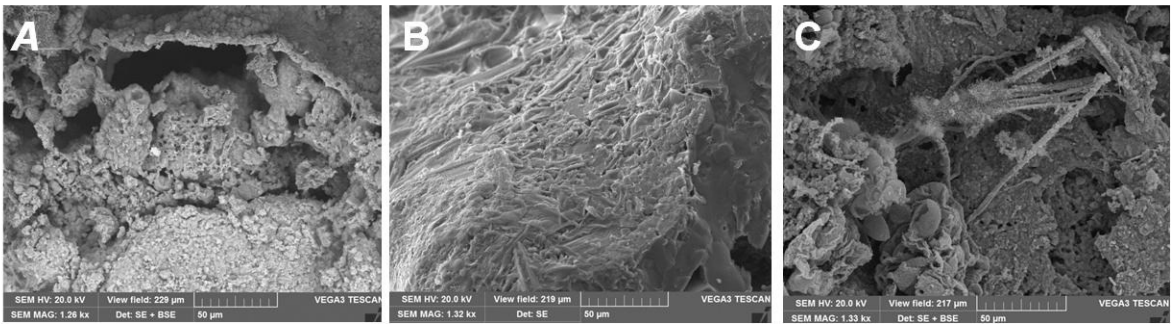

Fig. 6. SEM microphotographs after the SHS reaction: FIBERS-5 (A), FIBERS-6 (B) and FIBERS-7 (C), corresponding to the wt% waste reported in Tab. 2.

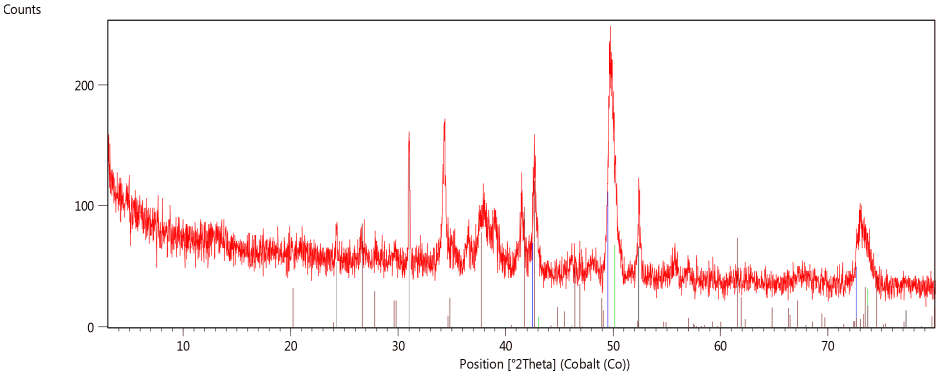

Fig. 7. Intensity pattern of the mineral aggregate composing sample FIBERS-6. Interpretation of the phases in the mineral mixture: olivine (red), MgO (green), FeO (blue)

Our treatment for asbestos-bearing waste is more effective than the state of the art both for time and energy costs: in fact, with the SHS method we could achieve asbestos conversion to olivine by applying 450° C preheating temperature for 300 seconds. The reaction was started with an oxyacetylene torch for few seconds, and propagated as self-sustaining reaction able to treat 500 grams of waste in 200 seconds. Anastasiadou K. et al. [4] obtained the same conversion of crumbly asbestos by a hydrothermal process lasting for 3 hours, at T between 690-800°C and P between 1.75 and 2.5 MPa. Gualtieri et al [7] used a conventional heat treatment, that needed T= 1100° C applied for 1 hour.

A laboratory experiment by Porcu et al. [13] is consistent with our results on friable fibers at larger scale. In the present experiment, the reaction did not decrease in efficiency, despite I) the use of a continuous process, II) an increased volume of treated waste and III) the use of industrial-grade reagents at lower degree of purity compared to those intended for laboratory use. Furthermore, the replacement of the priming white-hot tungsten coil with an oxyacetylene flame allowed a simplification of the apparatus, potentially facilitating a further industrial scale-up.

4. Conclusion

The inertisation of different types of ACW was tested by SHS combustion. The SHS combustion was applied satisfactorily to friable asbestos and fibre cement. We optimized the parameters to achieve complete conversion of the asbestos to mineral grains in both cases. The efficiency of the SHS reaction in the continuous configurations was highlighted by the characterization of the post-combustion material under SEM-EDS and XRPD that verified the absence of fibers.

The SHS process in comparison with conventional thermal treatments, due to fast reaction time, low activation energy, particularly advantages the asbestos inertisation and positively reflects into time and costs of the process.

In the perspective of the industrial implementation of the oven, the combustion, usually ignited by white-hot W coil, was also experimented with an oxyacetylene torch. This technique is efficient as for the energetic aspect and economically more sustainable.

Finally, the product of this transformation is liable to be re-used, e.g. as abrasive, or refractory material; this represents the end of waste status and a second life as secondary raw material.

Acknowledgements

This work was carried out in the frame of LIFE12 ENV/IT/000295 FIBERS co-funded by the European Commission awarded to University of Genoa (Coordinating beneficiary).

The authors acknowledge the collaboration of the UNIGE staff: Claudio Belfortini and Gigi Musi for the technical assistance, Laura Negretti for help in SEM mineral analyses acquisition, Cristina Carbone and Roberto Badano for XRPD analyses.

References

[1] Hannant PJ. Fibre Cements and Fibre Concretes. Chichester, Sussex, England: Wiley (John) & Sons; 1978

[2] Harris LV, Kahwa IA. Asbestos: old foe in 21st century developing countries, Sci Total Environ 2003; 307(1-3): 1-9

[3] Motion for a European Parliament Resolution on Asbestos related occupational health threats and prospects for abolishing all existing asbestos, 2012/2065 (INI).

[4] Anastasiadou K, Axiotis D, Gidarakos E. Hydrothermal conversion of chrysotile asbestos using near supercritical conditions. J Hazard Mater 2010; 179:926–932.

[5] Gadikota G, Natali C, Boschi C, Park AHA. Morphological changes during enhanced carbonation of asbestos containing material and its comparison to magnesium silicate minerals. J Hazard Mater 2014; 264:42–52.

[6] Viti C, Mellini M. Contrasting chemical compositions in associated lizardite and chrysotile in veins from Elba, Italy. Eur J Mineral 1997; 9:585–596.

[7] Gualtieri AF, Tartaglia A. Thermal decomposition of asbestos and recycling in traditional ceramics. J Eu Ceram Soc 2000;20;1409–1418.

[8] Plescia P, Gizzi D, Benedetti S, Camillucci L, Fanizza C, De Simone P, Paglietti F. Mechanochemical treatment to recycling asbestos-containing waste. Waste Manage 2003; 23:209–218.

[9] Sugama T, Sabatini R, Petrakis L. Decomposition of chrysotile asbestos by fluorosulfonic acid. Ind Eng Chem Res 1998; 37:79–88.

[10] Porcu M, Orrù R, Cincotti A, Cao G. Self-propagating reactions for environmental protection: Treatment of wastes containing asbestos. Ind Eng Chem Res 2005; 44,1:85–91.

[11] Gaggero L, Ferretti M, Belfortini C, Isola E. Metodo e apparato per l'inertizzazione di fibre di amianto, Italian Patent 2010; GE2010A000032.

[12] Munir ZA. Synthesis of high temperature materials by Self-Propagating Combustion methods. Amer Ceram Soc Bull 1988; 67:342–349.

[13] Gaggero L, Caratto V, Ferretti M. Asbestos fibers breakdown by Self-sustained High temperature Synthesis – SHS. J Env Manage 2016 (submitted)