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Self-Propagating Reactions for Environmental Protection: Treatment of Wastes Containing Asbestos

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A thermochemical process based on the occurrence of self-propagating reactions that is able to convert asbestos fibers into harmless, nonfibrous species is proposed. Specifically, a mixture consisting of a waste (containing about 85 wt % of chrysotile), ferric oxide, and magnesium is able, once locally ignited by a thermal source, to generate a self-propagating reaction that travels through the mixture without requiring additional energy. The process is accompanied by a dramatic change in the material from both the chemical and microstructural points of view. In addition, front velocity and maximum combustion temperature decrease as the amount of waste in the starting mixture increases, with the self-propagating character being maintained if the waste content is equal to or below 60 wt %. It is also observed that, when nonasbestos (nontoxic) materials, i.e., sepiolite and glass fibers, are used instead of the hazardous waste, the front velocity, combustion temperature, propagation limits, and apparent activation energies are found to be very similar to those observed in the case of asbestos.

1. Introduction

Asbestos materials have been extensively used in the past because of their useful properties for insulation and fireproofing.¹ However, because of the health hazard caused by respiration of their fibers, their use has been dramatically reduced in recent years.

It is known that the asbestos fiber size represents a critical characteristic, with the most dangerous being those characterized by lengths approximately in the range of 5–10 μm and diameters between 0 and 1 μm . In particular, fibers of chrysotile, which belongs to the class of serpentine minerals, have diameters in the range of 0.2–0.5 μm ¹ and, therefore, are considered particularly dangerous.

Several methodologies have been proposed for the treatment of materials containing asbestos. Specifically, they include resin coating,^{2,3} encapsulation with concrete,⁴ chemical attack,^{5,6} thermal treatments,^{7–9} and mechanochemistry.¹⁰ In addition, the dumping solution, which consists of properly disposing of the waste to prevent fiber dispersion, represents a partial and costly solution. The resin-coating method, where the material containing asbestos is covered by appropriate viscous substances to bond the fibers, thus avoiding their dispersion in the environment,^{2,3} can be considered a temporary solution because the problem of the potential dispersion of fibers still remains. The method based on the encapsulation of asbestos materials with concrete⁴ is relatively cheap, but the dispersion of fibers is still

possible, especially if the obtained product is subjected to mechanical stresses or chemical attack. Although the fibers can be destroyed by chemical attack with appropriate acids, for instance, fluorosulfonic acid,⁶ the use of such extremely aggressive substances is, to some extent, technically risky. On the other hand, because of the temperature levels of about 1000 °C or higher reached, thermal treatment and glassification processes are accompanied by the melting of the material and the consequent modification of asbestos microstructure.^{7–9,11} Therefore, the latter treatments seem to be the most effective as release of fibers is no longer possible, even if material degradation were to take place. The mechanochemical method, where asbestos wastes are converted into amorphous materials, can be also considered as a "cold" vitrification process.¹⁰

In this work, a new thermochemical method based on self-propagating high-temperature thermite reactions to render asbestos materials harmless is proposed. These kinds of reactions, typically exploited for the synthesis of materials by SHS (self-propagating high-temperature synthesis), are based on the concept that, once the starting mixture is ignited by means of external thermal sources for relatively short times, highly exothermic reactions can propagate in the form of a self-sustained combustion wave, progressively leading to final products without requiring additional energy.^{12–14}

The exploitation of self-propagating reactions for environmental protection purposes has also recently been considered as a possible alternative or complementary approach to traditional technologies of waste treatment. Specifically, interesting results have been obtained in the fixation and consolidation of high-level radioactive wastes,^{15–17} the treatment of zinc hydro-metallurgical wastes,^{18,19} the degradation of chlorinated aromatics,^{20,21} and the recycling of silicon sludge and aluminum dross produced by the semiconductor industry and aluminum foundries, respectively.^{22,23} A review

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Table 1. Properties of the Reactant Powders Used in the Treatment of Asbestos Containing Materials

component	vendor	size
Fe ₂ O ₃	Aldrich	<5 μm
Mg	Aldrich	-50 mesh
sepiolite [Mg ₄ Si ₆ O ₁₅ (OH) ₂ ·6H ₂ O]	-	30-60 μm
glass fibers	-	-

paper reporting the most interesting results in this field was recently published.²⁴

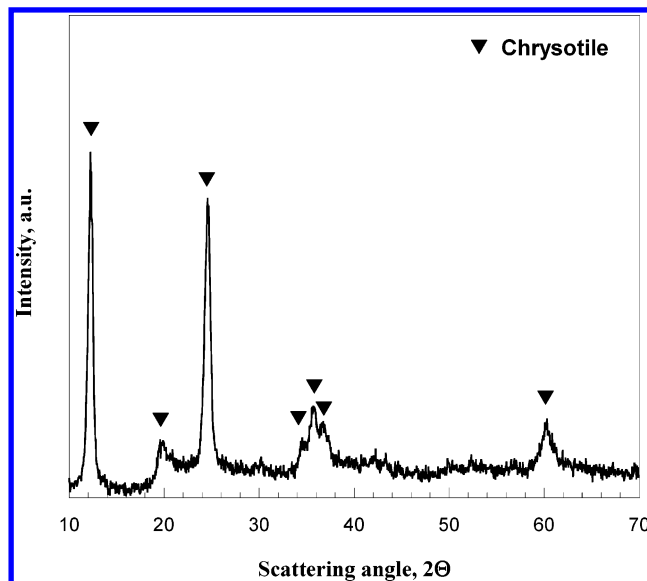
Along these lines, a novel approach for the thermochemical conversion of "asbestos-containing material" (ACM) based on self-propagating reactions is proposed in this work. In particular, preliminary tests using nonasbestos materials whose structure and properties are otherwise similar to those of chrysotile are carried out. Subsequently, the proposed treatment is applied to the hazardous waste. As explained in detail in the next sections of this paper, this approach is selected for sake of safety, to test reaction behavior of the combustion process. Specifically, a mixtures of glass fibers, to reproduce the fibrous structure, and sepiolite, to mimic the chemical composition of chrysotile, hereafter called "simulated asbestos-containing material" (SACM), is selected. Subsequently, the "real" ACM is subjected to the treatment, and the results obtained in this case are compared with those corresponding to the "simulated" material.

2. Experimental and Procedure

The experimental setup typically employed for the synthesis of materials by SHS²⁵ was used for the treatment of SACM and ACM wastes by self-propagating reactions. Briefly, it consists of a stainless steel reaction chamber filled with argon maintained at atmospheric pressure, a power supply that provides the energy required for reaction ignition, a video recorder for recording the evolution of the reaction, and a computer system that is used to drive the power supply to produce a well-defined energy pulse and for data acquisition purposes. The temperature during evolution of the reaction and the average velocity of the combustion wave were measured using thermocouples (W-Re, 127-μm diameter) embedded in the reaction mixture. During a typical experiment, the reaction mixture was placed into the vessel in the form of either cylindrical pellets or loose powders inside suitable stainless steel crucibles. The reaction was initiated by means of a tungsten coil connected to the power supply, which was programmed to produce an energy pulse at 20 V for about 4 s. This interval was selected so that the energy source was turned off as soon as the reaction was initiated. Reproducibility was guaranteed by repeating each experimental run at least twice.

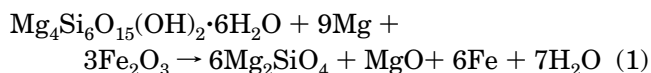
As mentioned in the Introduction, preliminary tests are carried out using materials (SACM) whose structure and properties are similar to those of chrysotile, i.e., Mg₆(Si₄O₁₀)(OH)₈. Specifically, mixtures of glass fibers and sepiolite, i.e., Mg₄Si₆O₁₅(OH)₂·6H₂O, are used. The former was chosen to simulate the fibrous structure of chrysotile, while sepiolite was selected to mimic its chemical composition.

Glass fibers and sepiolite were blended with suitable amounts of magnesium and ferric oxide. The available properties of all reactants used are reported in Table 1. The molar ratio between magnesium and ferric oxide

**Figure 1.** XRD pattern of asbestos containing material.**Table 2. Composition (wt %) of the Mixtures Investigated**

sample ID	ferric oxide	magnesium	sepiolite	glass fibers	ACM
40 SACM	41.2	18.8	20	20	-
50 SACM	34.3	15.7	25	25	-
60 SACM	27.4	12.6	30	30	-
70 SACM	20.6	9.4	35	35	-
40 ACM	41.2	18.8	-	-	40
50 ACM	34.3	15.7	-	-	50
60 ACM	27.4	12.3	-	-	60
70 ACM	20.6	9.4	-	-	70

adopted during the experiments was chosen according to the following reaction



It is worth noting that the thermite reaction between ferric oxide and magnesium to form magnesium oxide and iron is strongly exothermic,²⁶ so that the presence of these two reactants makes the self-propagating process based on reaction 1 feasible.

The compositions of the mixtures investigated are shown in Table 2.

As reported in the same table, mixtures containing amounts of ACM equal to those of SACM were subjected to the same treatment. Specifically, the ACM selected for the investigation was a millboard product used for heat insulation containing about 85 wt % of chrysotile. The corresponding XRD pattern is reported in Figure 1. It can be seen that the only crystalline phase detected in this material is chrysotile.

Sample handling, i.e., blending, pelletizing of the reaction mixture, and treatment based on self-propagating reactions, was carried out in strictly controlled containment to avoid any fiber dispersion in the environment.

Characterization of all samples before and after treatment to verify the compositional and microstructural changes was performed by X-ray diffraction (XRD) (Philips 1830 diffractometer using Cu Kα Ni-filtered radiation), scanning electron microscopy (SEM) (Hitachi S 4000 field emission), and electron dispersive spectroscopy (EDS) (Noran Instruments Inc., KEVEX SIGMA 32 probe at a resolution of 142 eV).

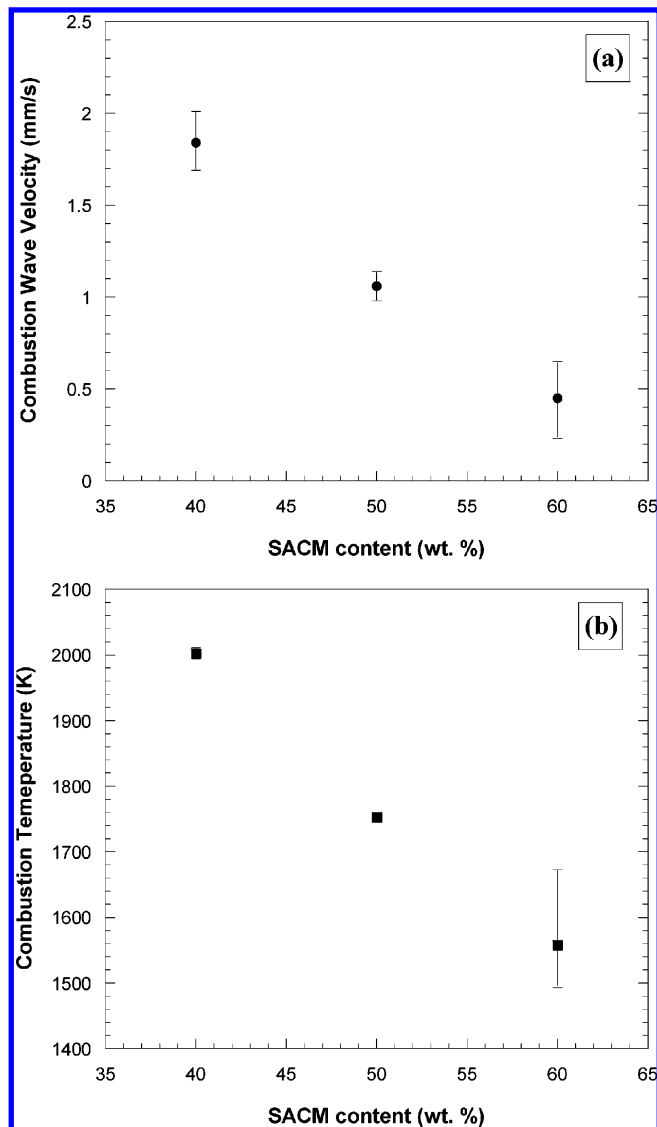


Figure 2. Dependence of (a) wave velocity and (b) maximum combustion temperature on SACM content in the starting mixture.

3. Results and Discussion

The treatment of the ACM wastes was preceded by an investigation in which the dangerous material was replaced by a nontoxic mixture that however, has analogous compositional and structural properties. This preliminary study was performed to verify the feasibility of the combustion process in terms of mixture reactivity as well as to evaluate process safety. This choice is related to the similarity in chemical composition between sepiolite and chrysotile, which might lead to analogous combustion process dynamics (possible explosive behavior, combustion temperature, wave velocity) in the two cases. Moreover, the addition of glass microfibers had the objective of verifying the capability of the treatment to destroy the fibrous structure present in the starting mixture.

The reaction behaviors of the mixtures in terms of the average combustion wave velocity and maximum temperature recorded during combustion process evolution are reported in Figure 2a and b, respectively. Regarding the conditions needed for establishment of the self-propagating regime in the reacting system, it was found that, if the content of SACM in the starting mixture was equal to or lower than 60 wt %, the mixture

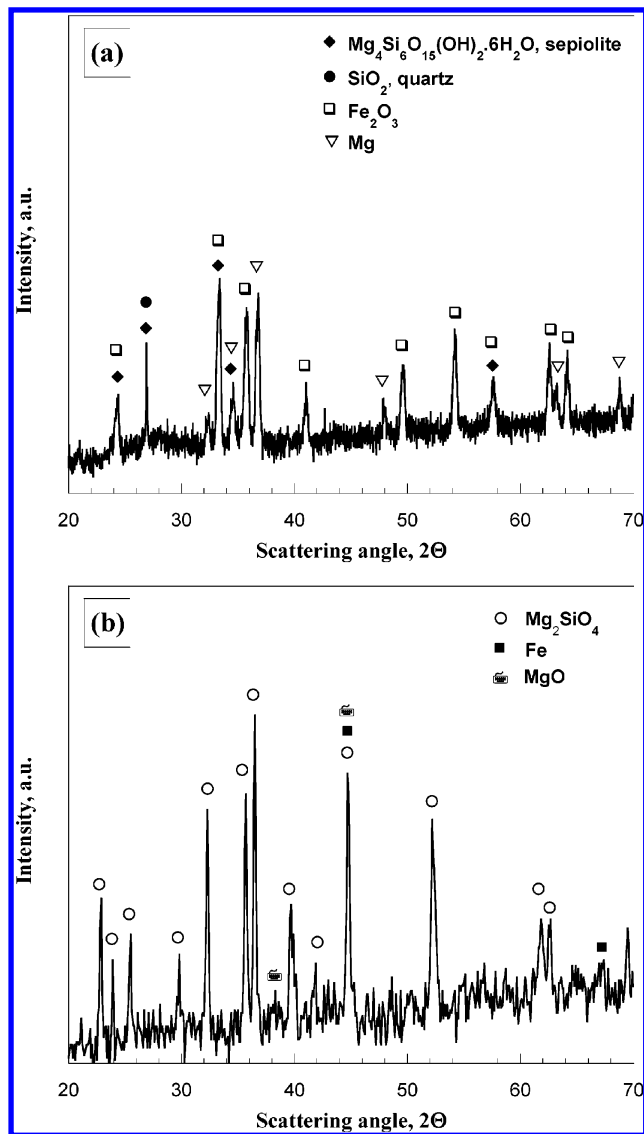


Figure 3. XRD patterns of sample 60SACM: (a) starting mixture and (b) product after treatment.

was characterized by SHS behavior. In addition, the figure shows that both wave velocity and temperature values decrease with increasing SACM content as a consequence of the fact that the exothermicity of the starting mixture decreases. In particular, waste amounts equal to or greater than 70 wt % correspond to mixtures that are not able to self-propagate. A weight loss of about 10 wt % in the solid mixture was observed during the proposed treatment. This result is consistent with the formation of water according to the stoichiometry of reaction 1. It is also worth noting that no explosive character of the reaction was observed in the entire range of the SACM amounts investigated. Moreover, no expulsion of powders, including fibers, was observed to occur during evolution of the reaction. Thus, the process can be considered safe in operation.

Regarding the effect of the treatment on product characteristics, the XRD patterns and SEM micrographs of the starting pellets are compared with the corresponding ones of final products in Figures 3 and 4, respectively, both referring to the mixture identified by 60 SACM in Table 2. From the XRD analysis, it is clearly apparent that the initial mixture (a) is completely converted into a product (b) constituted only by forster-

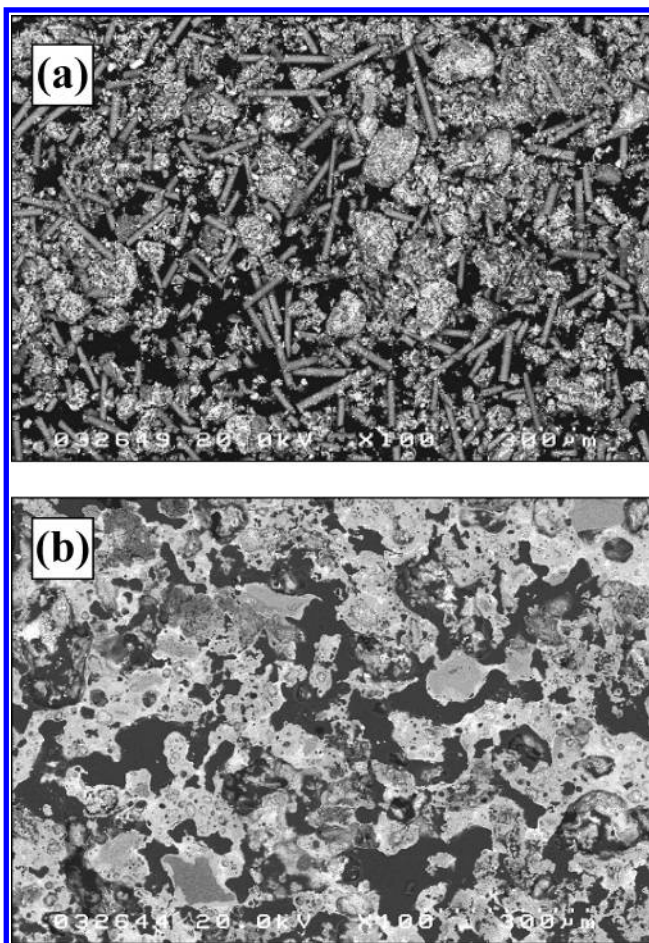


Figure 4. Backscattered SEM micrographs of sample 60SACM: (a) starting mixture and (b) product after treatment.

ite (Mg_2SiO_4), magnesium oxide, and iron. It is worth noting that this result is perfectly consistent with reaction 1.

In addition, from the micrographs shown in Figure 4, it can be observed that the fibers, which can be easily identified in the micrograph of the starting sample (cf. Figure 4a), are totally destroyed after the treatment (cf. Figure 4b). This is a consequence of both the chemical transformation occurring during the process and the melting phenomenon taking place because of the high temperatures reached, which completely changes the structure of the starting material.

A similar behavior was also observed for the other mixtures investigated (cf. Table 2).

Consequently, the results obtained with preliminary tests, where asbestos-like materials are subjected to the treatment based on self-propagating reactions, showed that the proposed process seem to be very promising for rendering asbestos materials harmless in terms of safety and the characteristics of the final product.

Figure 5a and b shows the dependences of the wave velocity and combustion temperature on the content of material containing asbestos in the starting mixture. The boundary limit of ACM content below which the reacting system displays SHS behavior is 60 wt %, i.e., the same value found when employing SACM. Moreover, both the reaction front velocity and the combustion temperature decrease as the amount of chrysotile in the mixture increases, thus following a similar behavior as for the case of the SACM. The analogy is satisfactory from the quantitative point of view as well. This aspect

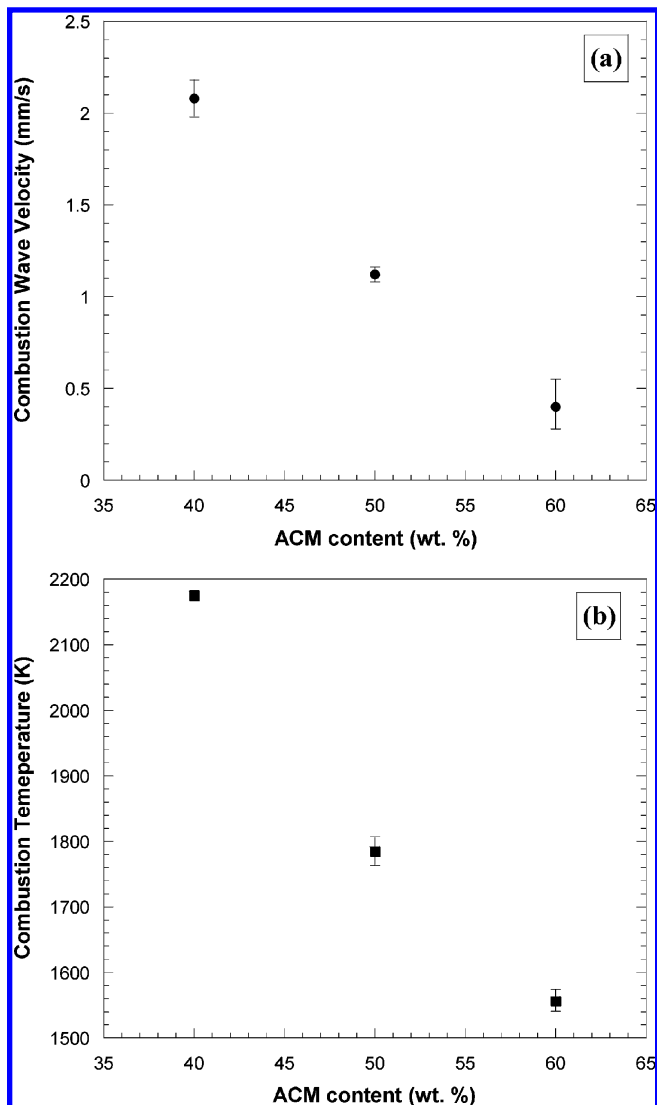


Figure 5. Dependence of (a) wave velocity and (b) maximum combustion temperature on ACM content in the starting mixture.

also holds true regarding the weight losses of about 10 wt % observed after reaction, which are due to water formation.

The effect of the treatment on the composition of the final product as compared to that of the corresponding starting mixture can be seen in Figure 6a and b, where the XRD analysis results are reported for the case of 50ACM. It is apparent that the chrysotile reflections found in the XRD pattern related to the initial mixture completely disappear after treatment. Moreover, as in the case of SACM, forsterite, magnesium oxide, and iron are the only crystalline phases detected in the product.

The complete destruction of the fibrous structure of chrysotile caused by the proposed treatment can be observed in Figure 7a and b, where the SEM micrographs of the starting mixture and the final product, respectively, are reported. This result is representative of all mixtures investigated where the self-propagating reaction was observed to occur.

It is well-known that, in the field of self-propagating reactions, analytical expressions of the velocity of the combustion front as a function of the various system parameters (i.e., heat of reaction, thermal conductivity, adiabatic temperature, and activation energy) have been proposed.^{27–31} These expressions are typically obtained

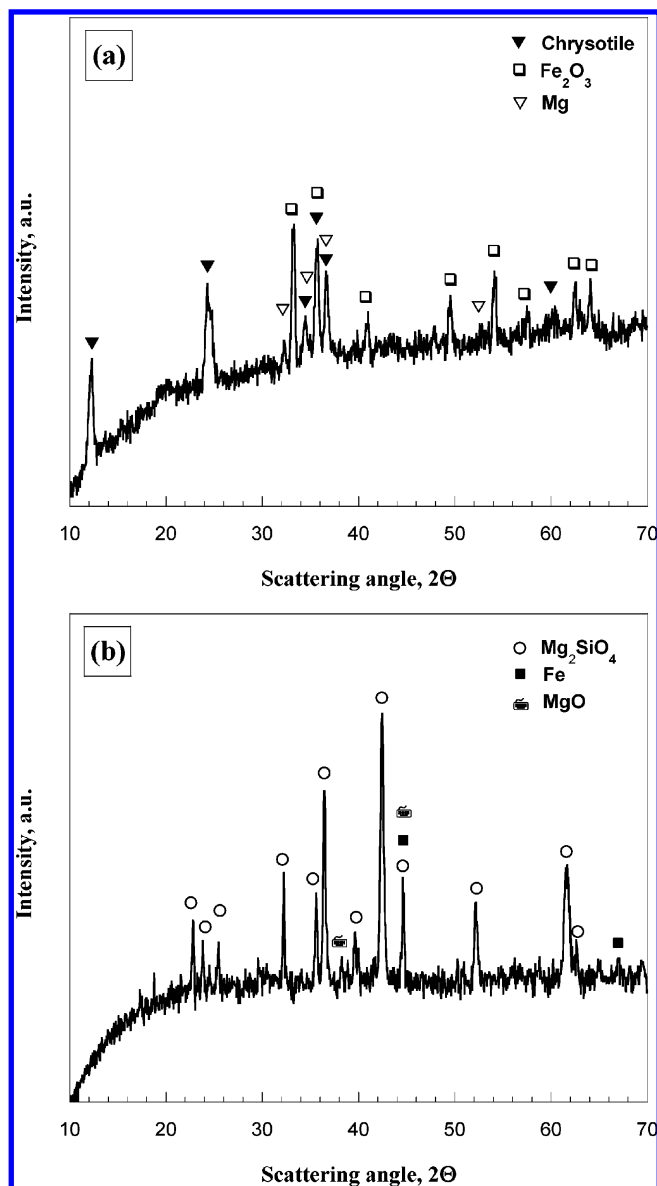


Figure 6. XRD patterns of sample 50ACM: (a) starting mixture and (b) product after treatment.

under the assumption of adiabatic conditions as well as constant pattern, i.e., the combustion front propagates at a constant velocity, and the Frank–Kamenetskii approximation.²⁷ In the case of first-order-type kinetics, the following expression for the front propagation velocity holds

$$v^2 = \frac{k}{(-\Delta H_r)\rho} \frac{RT_c^2}{E} k_0 \exp\left(-\frac{E}{RT_c}\right) \quad (2)$$

where T_c is the combustion temperature, R is the gas constant, ρ is the density, k is the thermal conductivity, $-\Delta H_r$ is the heat of the reaction, k_0 is the kinetic constant, and E is the apparent activation energy of the process. Plots of $\ln(v/T_c)$ as a function of $1/T_c$ are typically employed to calculate the activation energy in accordance with eq 2. Such plots are shown in Figure 8 for the self-propagating reactions of SACM and ACM. The resulting activation energies, obtained from the slopes of the two plots, are equal to 67.4 and 58.9 kJ/mol for SACM and ACM, respectively. Activation energy values determined from such calculations can be as-

sociated with a certain combustion mechanism taking place during evolution of the reaction. Although such an investigation is beyond the scope of this work, it is apparent that the estimated values are fairly similar, thus confirming the analogous combustion behaviors of the two mixtures under investigation, at least within the range considered in this work. This aspect can be related to the predominant effect of the thermite reaction between Fe_2O_3 and Mg, whose quantities are maintained the same in both systems as can be seen in Table 2. In fact, because of its strong exothermicity, such a reaction is most likely responsible for guaranteeing the self-propagating character of the process.

Concluding Remarks

A thermochemical process able to convert asbestos fibers into harmless, nonfibrous species is proposed. Specifically, it is seen that, after blending in appropriate proportions a waste containing about 85 wt % of chrysotile with ferric oxide and magnesium, the resulting mixture is able, once locally ignited by a thermal source, to generate a combustion wave that self-propagates without requiring the input of additional external energy. The process is accompanied by a dramatic change in the material from both the chemical and microstructural points of view. Although the practical utilization of the obtained combustion product has not been investigated, it could be employed, for example, as an inert material in combination with concrete in the building industry, as the release of fibers is no longer possible.

It is found that reaction front velocity and maximum combustion temperature reached during the process decrease as the amount of the waste in the starting mixture increases. In particular, the self-propagating character is maintained if the ACM content is equal to or below 60 wt %.

From an economic point of view, the proposed method exhibits all of the advantages (the relatively short processing time, the occurrence of self-heating to high temperatures instead of external heating, the absence of external heating elements and the simplicity of the required equipments) of SHS processes over conventional thermal treatments. In addition, regarding the employment of commercial additives (Fe_2O_3 and Mg) to be mixed with the waste to make the reaction mixture self-propagating, it is worth noting that the possibility of totally or partially substituting them with analogous industrial scraps was recently demonstrated by considering different wastes.³² Moreover, the proposed treatment can be carried out in a battery of small, easy-to-use SHS reactors, as already proposed for the case of zinc hydrometallurgical wastes.^{19,33} It should be noted that a combustion behavior, i.e., combustion temperature and front velocity, similar to that pertaining to the latter system has been found. Therefore, regarding scale-up aspects, considerations analogous to those reported by Cincotti et al.³³ can be made. Treatment safety can be guaranteed by the fact that the process occurs in a closed and limited volume.

On the basis of the results and considerations reported in this work, it seems apparent that the technique described above clearly represents a method in which asbestos-containing materials can be easily altered from the compositional and structural points of view, thus allowing their safe disposal.

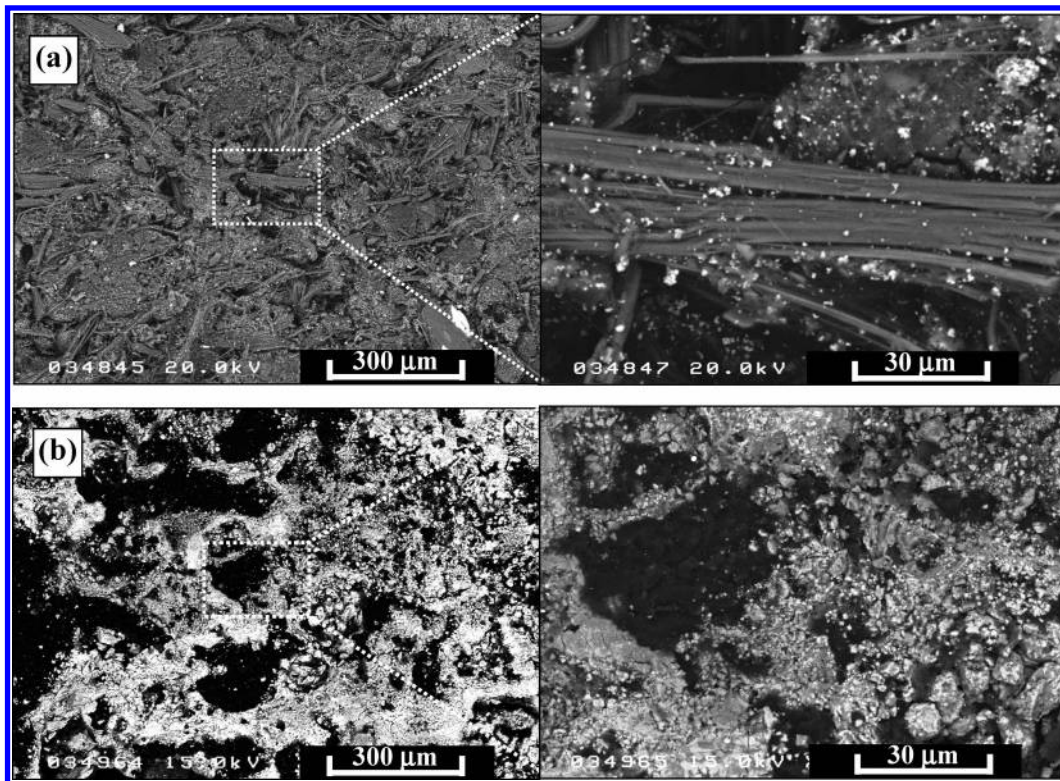


Figure 7. General and detailed backscattered SEM micrographs of sample 50ACM: (a) starting mixture and (b) product after treatment.

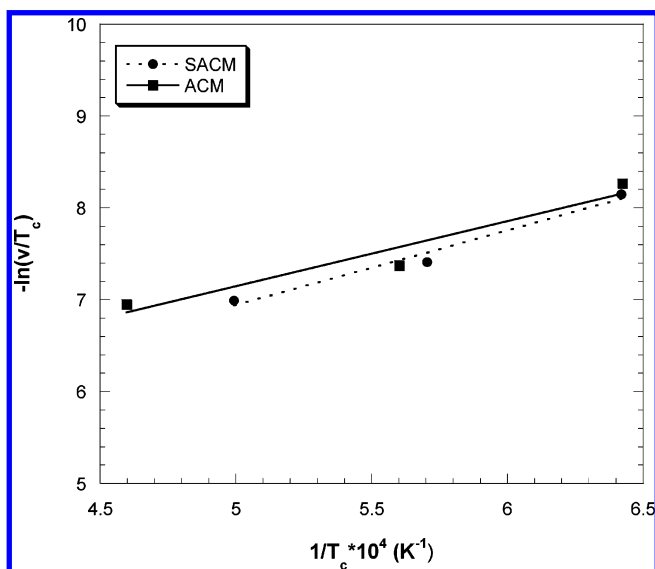


Figure 8. Arrhenius plots of $\ln(v/T_c)$ vs $1/T_c$ for the SACM and ACM systems.

In addition, it is also observed that, when nonasbestos (nontoxic) materials, i.e., sepiolite and glass fibers, are used instead of the hazardous waste, the front velocity, combustion temperature, propagation limits, and apparent activation energies are found to be very similar in the two cases. It should be noted that the evaluation of the apparent activation energy for ACM was not aimed at correlating this value with a specific reaction mechanism. However, it can be profitably used for SHS reactors design purposes, either using simplified front propagation velocity expressions or more structured reactors models, as recently shown in the literature.³³

Finally, it should be pointed out that the demonstrated analogous SHS behavior of ACM and SACM clearly identifies SACM as a safe-to-use material that

mimics the hazardous one. This finding allows one to perform less expensive and safer experimental campaigns as employing stringent precautions and making use of specific equipped laboratories are not required.

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