Hydrothermal process development for treatment asbestos containing waste

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Summary:

The asbestos containing waste management is a public health topic for countries which have used this mineral. Treatment of chrysotile, crocidolite and asbestos containing waste conversion process is proposed by using hydrothermal treatment in supercritical water. All samples were treated in an inconel batch reactor. Maximum treatment duration is 6 *h*, for temperatures in the range (400°C≤T≤750°C), mass concentration (0.02-170 mg/ml) and P≥23 MPa. Ultrapure water is used for sample preparation. Transmission electron microscopy analysis were carried out to identify persistence or asbestos disappearance. According to these analysis, optimal conditions of conversion were (t=1h; C=0.02 mg/ml) for chrysotile, (t=3h; C=0,02mg/ml) for crocidolite and (t=1h; C=20 mg/ml) for asbestos containing waste, with T=750°C. Supercritical water conditions was maintained during the treatment. The X-ray diffraction showed that the main phases present after treatments were riebeckite and magnetite (crocidolite), forsterite and enstatite (chrysotile), calcite, spurrite and gehlenite (asbestos containing waste). Finally, scanning electron microscopy analyse was performed to monitor morphological fiber change. The elongated structure partially fragmented was founded in all samples.

Key words: chrysotile, crocidolite, asbestos containing waste, hydrothermal treatment, supercritical water

I- Introduction

Since antiquity, asbestos is used for material manufacture [1]. More recently in the 19th century, thanks to its good thermal, acoustical, electrical insulation, chemical resistance attack (acid, base) and non-biodegradable properties, asbestos was applied to industrial application. Mix with cement, it allows fibrocement manufacture widely used in building industry. However, studies indicated the development of diseases (mesothelioma, asbestosis) due to asbestos exposure [2, 3]. Since 1997, asbestos is prohibited in France and all products containing asbestos were defined as hazardous. Therefore, hazardous waste quantity increases to reach 190 000 t/year according the Europlasma reference document 2016.

According report of data on the waste field in relation to the treatment ways available, communicated by BRGM in 2017, French's disposal landfill is limited by discharge places saturation. Plasma torch vitrification [4], an expensive and energetic process, is the only way to eliminate asbestos containing waste (ACW). Thermal, chemical and thermo-chemical technologies were developed at laboratory scale. Gualtieri, Viani and Kusiorowski [5-7] have proposed to decompose chrysotile, crocidolite and tremolite in a calcination furnace below melting temperature (T≤1200°C). Decomposition is carried out in two steps: crystalline phase rearrangement and subsequent dehydroxylation. Other thermal technologies, as microwave process have been reported [8-10]. Thermal processes can eliminate ACW into non-hazardous material but remain very expensive regarding energy consumption.

Pure chrysotile has been decomposed at low temperature by solid-gas reaction [11]. The acid gas (HCl and HF) was obtained by Freon decomposition. Hyatt [12] and Rozalen [13] used strong acid and organic acid to convert chrysotile in amorphous material. Same product is obtained by using lichens bio organism lichens [14, 15]. This latter secretes oxalic acid which leaches brucite layer of chrysotile. The hazardous effluent management with long time treatment are the main limitations of chemical treatments.

Chrysotile conversion is possible by using hydrothermal treatment [16-19]. It is realized in a high pressure autoclave under sub or supercritical water environment, with low time treatment and temperature $T \leq 800°C$. This process produces less hazardous effluent management than chemical processes. Energy consumption is lower than for thermal processes. The main object of this research is to evaluate and develop the feasibility of chrysotile, crocidolite and ACW conversion in non-hazardous material under hydrothermal conditions.

II- Methods and Materials

Sample

Several asbestos varieties were used for experimental test. The canadian chrysotile B (1.0 g) and south african crocidolite (0.1 g) from Koegas mine and bulk ssbestos analytical standard sample IUCC was supplied by SPI-Chemical. Pure chrysotile was grade 4 on the canadian scale. ACW is recovered on a building site. The chrysotile content was determined to be 0.4 mass % by using transmission electron microscopy (TEM) analysis in a public institution with Cofrac French accreditation. It was milled into a crusher 14 premium line a registered trademark of Fritsch Company, which contained an 80 µm screen ring. Ultrapure water produced by milli-Q direct system is used for sample preparation.

Apparatus

A reactor (inconel 718, 100 ml, 750°C, 30 MPa, Top Industries, France) resisting tocorrosive attack in supercritical conditions is used. It can work up to temperature of 750°C and pressure of 30 MPa. Reactor control is done with labview software. The whole set-up is illustrated in Figure 1. A stainless steel beaker of 50 ml is used to confine asbestos suspension in the autoclave.

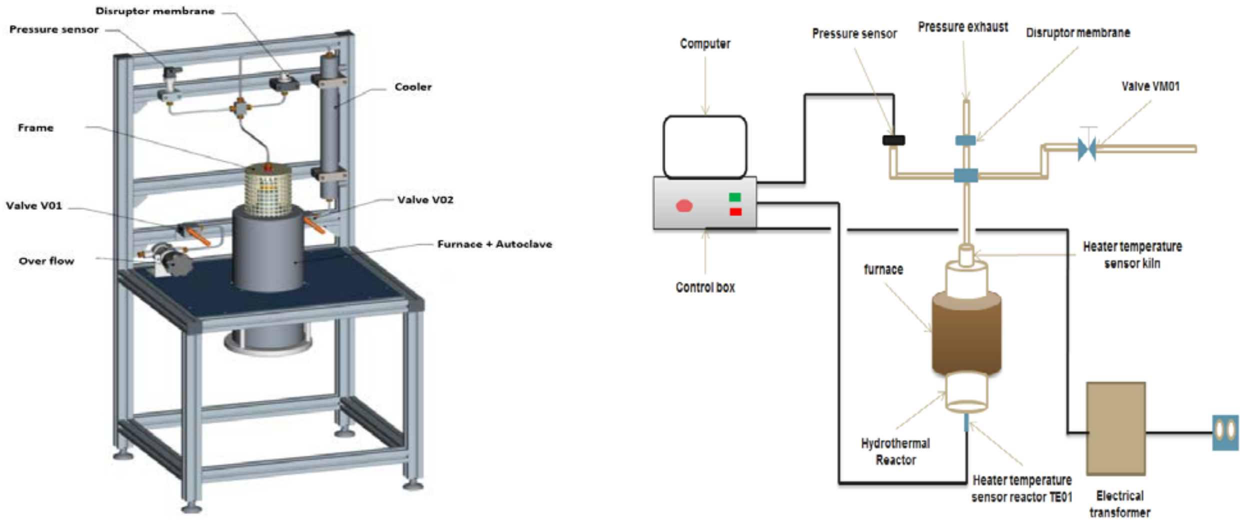


Figure 1: Experimental set-up for hydrothermal treatment

Procedure

Sample were prepared by adding ultrapure water to asbestos previously weighed balance Mettler Toledo, XS205DU model). The sample is introduced in the beaker, inserted into the autoclave and placed in the furnace. The heating conditions were monitored continuously. Final pressure depends on sample volume introduce into reactor. Reactor is cooled down at room temperature, and products were recovered by using ultrapure water. Five rising cycle with 10 ml of ultrapure water are realized. A sample of 50 ml is obtained. Several sub-samples were prepared for analysis. One sub-sample is filtered by polycarbonate filter and submitted to SEM (Zeiss Ultra 55, x1000-x50000 Magnification, SE2-Inlens Detectors, 8 mm focal, 20-60 µm diaphragm, 5-10 keV) analysis, in order to investigate the morphological changes. Crystalline phase (XRD, Panalytical X'PERT PRO, MPD model, radiation CuKα, graphite monochromator, collecting step 0.033, scanning speed 359.9°/s, 2θ= 4.801-111°, 45 kV, 40mA, 1800 W) were identified before and after hydrothermal treatment on solid residue recovered after nylon filtered sub-sample. Last sub-sample was conditioned and expedited to an external laboratory accredited cofrac (French accreditation) to identify persistence or not of asbestos crystalline phase by using TEM Analysis. According to NF X 43 050, TEM analysis is based on three criteria:
-morphology: hazardous fiber is defined for length L≥5 µm; a diameter 0.01≤D≤3 µm; ratio L/D≥3;
-electron diffraction analysis: to identify and compare with 6 asbestos standard spectrums, according regulation;
-electron dispersive X-rays spectrometry: for a comparative chemical composition between standards asbestos and identify particle spectrums.

III- Results

In the hydrothermal conditions of this study, water penetrates asbestos to induce brucite hydrolysis layer [17]. For Sigon [19], denaturation is based on dehydroxylation of chrysotile followed by a crystalline structure modifications in forsterite and silica leached by-products (equation 1).

$$2\,Mg_3Si_2O_5(OH)_4 \rightarrow 3\,Mg_2SiO_4 + 2\,SiO_{2(aq)} + 4\,H_2O \qquad (1)$$

According to Kozawa [18], forsterite can transformed in enstatite crystallite. This mechanism is illustrated by equations 2 and 3:

$$2\,Mg_3Si_2O_5(OH)_4 \rightarrow 3\,Mg_2SiO_2 + SiO_2 + 4\,H_2O \tag{2}$$

$$Mg_2SiO_2 + SiO_2 \rightarrow 2Mg_2SiO_3 \tag{3}$$

Chrysotile, crocidolite and ACW samples are treated. Chrysotile was the most asbestos variety used for industrials application in France. According to asbestos guide management, chrysotile represented 90% of France asbestos imports. For this reason, hydrothermal process is applied mainly on this asbestos variety. Then, crocidolite and ACW was respectively denatured. The process conditions (temperature, time of treatment and mass concentration material/water) of hydrothermal conversion are detailed on (Table 1).

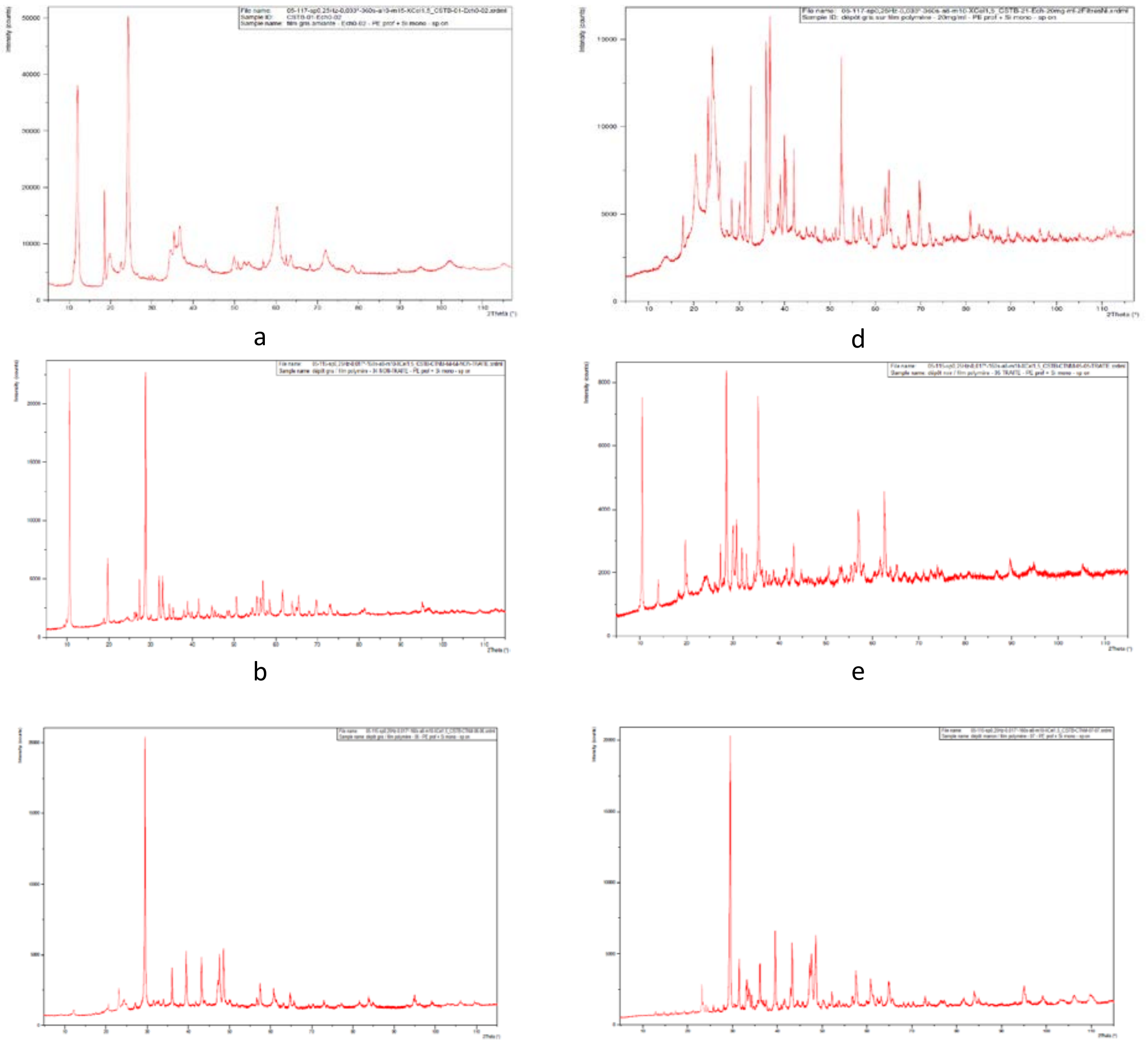
Table 1 : TEM Analysis results for hydrothermal treatment

Sample	Temperature (°C)	Pressure (MPa)	Time (min)	Mass concentration (mg/ml)	TEM Analysis
Chrysotile	400	26	60	0.021	chrysotile
Chrysotile	500	26	60	0.022	chrysotile
Chrysotile	750	28*	10	0.023	chrysotile
Chrysotile	750	27*	30	0.022	chrysotile
Chrysotile	750	27	60	0.022	chrysotile
Chrysotile	750	27	180	0.020	chrysotile disappearance
Chrysotile	750	26	360	0.021	chrysotile disappearance
Crocidolite	750	26	60	0.023	crocidolite
Crocidolite	750	24	180	0.020	crocidolite disappearance
Crocidolite	750	26	360	0.020	crocidolite disappearance
ACW	750	26	60	2	chrysotile disappearance
ACW	750	26	60	20	chrysotile disappearance
ACW	740	26	360	20	chrysotile disappearance
ACW	740	23	360	170	chrysotile disappearance

*High pressure

The TEM analysis (Table 1) for all treatment conditions show a chrysotile and crocidolite disappearance after 1 and 3 h of thermal treatment, for a temperature of T=750°C, a mass concentration of 0.02 mg/ml and pressure of 26 MPa. The chrysotile conversion conditions (T=750°C; P=26MPa) applied on ACW shown the mass concentration 20 mg/ml can be converted in non-asbestos waste after 1h time treatment.

Also, for temperature above 500°C, chrysotile crystalline structure always persists, despite supercritical environment. Probably, activation energy is not yet reached to initiate structural transformation.



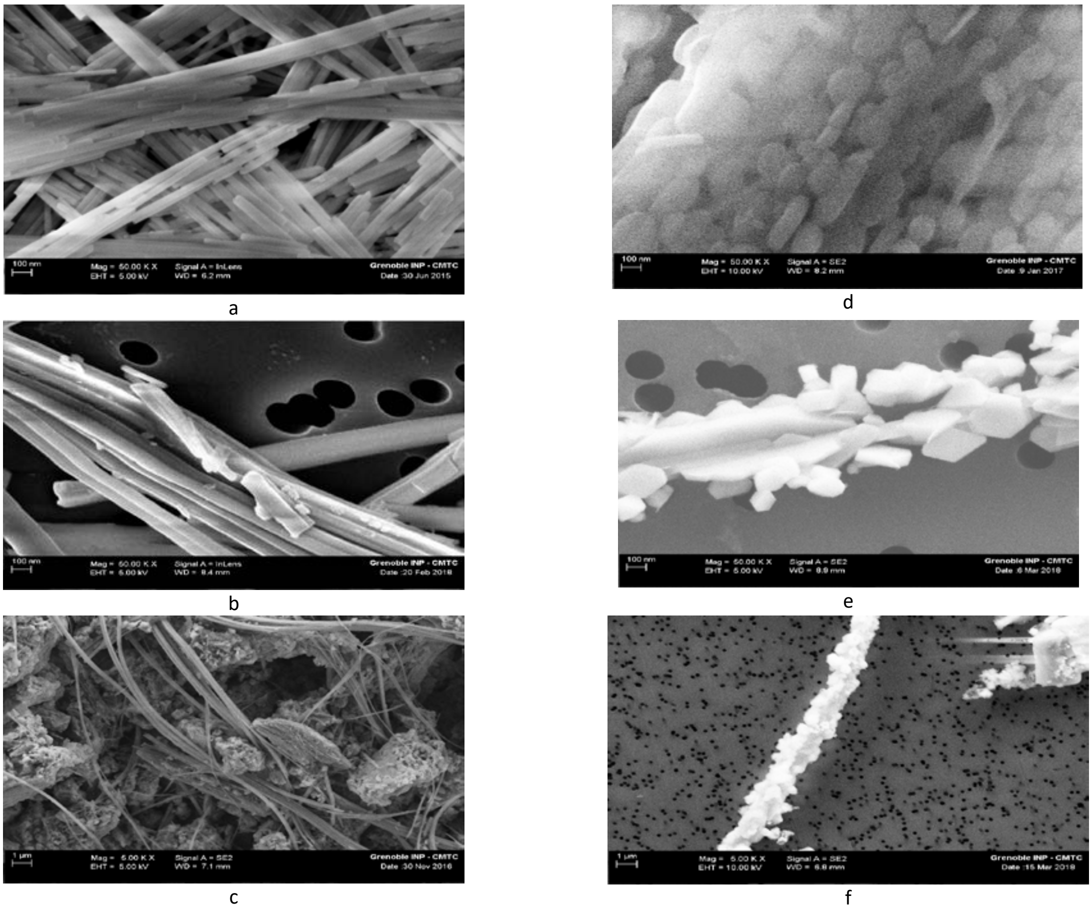
a d

b e

c f

Figure 2 : XRD spectrum of chrysotile, crocidolite and ACW (a, b, c) before and after (d, e, f) hydrothermal treatment

A total conversion of chrysotile in forsterite and enstatite is observed in Figure 2. The XRD spectrum of pure chrysotile (a) present two characteristic peaks, respectively (2ϴ=12.1° and 2ϴ=24.4°)[18]. After hydrothermal treatment (T=740°C; P=26 MPa; C=20mg/ml; t=6h), these peaks have not been detected in spectrum XRD. Only forsterite (Mg_2SiO_4) and enstatite (Mg_2SiO_3) crystallites are detected (d). Riebeckite, a crocidolite usual name was founded before (b) and after (e) hydrothermal treatment (T=750°C; C=1mg/ml; t=3h), while TEM Analysis showed a total conversion for treatment conditions (T=750°C; C=0.02 mg/ml; t=3h). This XRD result is probably due to the mass concentration difference. Indeed, a minimum amount (1 cm^3 thickness) of mineral is required to perform XRD analysis, as opposed to TEM Analysis based on fiber by fiber detection which require less material. Calcite, vaterite ($CaCO_3$) and chrysotile ($Mg_3Si_2O_5(OH)_4$) are the majority phases founded in the ACW non-treated (c) hydrothermally. After 6 hours of time treatment, a temperature T=750°C, C=20 mg/ml and P=27 MPa, the calcite, spurrite ($Ca_5(SiO4)_2(CO_3)$) and gehlenite (Ca2Al2SiO7) are detected in XRD spectrum (f). The ACW is totally converted in non-asbestos waste.



a d b e c f

Figure 3: SEM picture of chrysotile, crocidolite, ACW before (a, b, c) and after (d, e, f) hydrothermal treatment

Elongated structure obtained in chrysotile and crocidolite crystalline transformation present a fragmented appearance (Figure 3). Nevertheless, in low magnification (X1000), fibrous skeleton still remains. To be in accordance with regulation on hazardous morphology criteria, an elongated structure fragmentation by using ultrasound post-treatment could be considered as in Park, Sawawi and Lucas [20-22]. Indeed ultrasonication is could be able to reduce long fiber in small size particle and further characterisation and experiments should be done on hydrothermal products.

Conclusion

According to the result obtained, hydrothermal process applied for crystalline conversion of chrysotile, crocidolite and asbestos containing waste treatment is efficient. However, elongated structures persist after treatment. The advantages of this technology are:

- The low energy consumption than thermal processes which are realized for T ≥ 1200°C, especially torch plasma vitrification.
- No additive chemical solution are used for conversion chrysotile, crocidolite and ACW in non-hazardous waste
- To able to convert simultaneous asbestos and organics waste by using supercritical water oxidation

In all hydrothermal treatment article applied pure asbestos (chrysotile, crocidolite), no mechanism conversion is clearly defined and admitted by scientific community to describe hydrolysis transformation.

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