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Hydrothermal process development for treatment asbestos containing waste

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I- Introduction

Since antiquity, asbestos is used for material manufacture [1]. More recently in the 19th century, for 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 have shown diseases (mesothelioma, asbestosis) due to asbestos exposure [2, 3]. Since 1997, asbestos is prohibited in France and all products containing asbestos was defined as hazardous. Therefore, hazardous waste quantity increases to reach 190 000 t/year (Euro plasma 2016).

According legislation, disposal landfill is limited by discharge places saturation (BRGM 2017) and plasma torch vitrification [4], an expensive and energetic process, is the only way to eliminate Asbestos Containing Waste (ACW). Few thermal, chemical and thermo-chemical technologies were developed at laboratory scale. Gualtieri, Viani and Kusiorowski [5-7] have proposed chrysotile, crocidolite and tremolite decomposition in a calcination furnace below melting temperature ($T \leq 1200°C$). Decomposition 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 eliminated ACW into non-hazardous material, but remain very expensive for energy consumption.

Pure chrysotile has been decomposed at low temperature by solid-gas reaction [11]. This acid gas (HCl and HF) was obtained by Freon decomposition, while 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 secrete 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 carried out in high pressure autoclave under sub or supercritical water environment, with low time treatment and temperature $T \leq 800°C$. This process is more ecological than chemical processes, which are limited by hazardous effluent management. Also, energy consumption seems to be 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 Asbestos Analytical standard sample IUCC was supplied by SPI-Chemical. Pure chrysotile was Grade 4 on the Canadian scale. Asbestos Containing Waste (ACW) is recovered on a building site. The chrysotile content was determined to be 0.4 mass % by using MET analysis in a public institution with Cofrac French accreditation company. It was milled into a Pulvérisette 14 premium line of Fritsch grinder, which contained an 80 µm screen ring. Ultrapure water produced by milli-Q direct system is used for sample preparation.

Apparatus

An Inconel 718 reactor (100 ml, Top Industry, France) allowing to work under sub (T≤400°C; P<22.1 MPa) and supercritical steam (T≥400°C; P≥22.1 MPa) is carried out for chrysotile, crocidolite and ACW conversion. It resists at corrosive attack in supercritical conditions. It can work at 750°C and a pressure of 30 MPa. Reactor control is done from labview software. The control box provides communication between the test bench and the software, illustrated by (Figure 1). A stainless steel beaker of 50 ml is used to confine asbestos suspension.

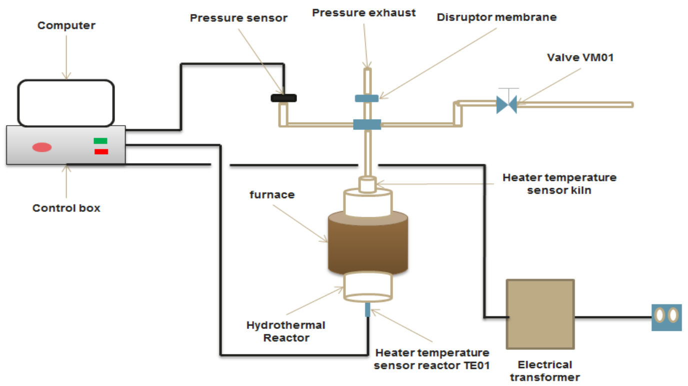


Figure 1: Experimental process diagram for hydrothermal treatment

Procedure

Asbestos sample was prepared by adding ultrapure water filtered in a quantity of asbestos previously weighed with an analytical balances (Mettler Toledo, XS205DU model). This sample is introduced in the stainless steel beaker, inserted into the autoclave and placed in the furnace. The heating conditions were monitored by controller, and pressure measurement depends on sample volume introduce into reactor. After reactor is cooled at room temperature, the mixture was recovered by using ultrapure water. Five rising cycle with 10 ml of ultrapure water is realized. A sample of 50 ml is obtained. Several sub-samples were prepared for characterisation analysis. One sub-sample is filtered by polycarbonate (PC) 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 Cofrac Company to identify persistence or no asbestos crystalline phase by using MET analyse.

III- Results

In hydrothermal environment, supercritical steam 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 by-product, which can transform in enstatite. This mechanism is illustrated by two equations [18] :

$$2\,Mg_3Si_2O_5(OH)_4 \rightarrow 3\,Mg_2SiO_2 + SiO_2 + 4\,H_2O \qquad (1)$$

$$Mg_2SiO_2 + SiO_2 \rightarrow 2Mg_2SiO_3 \qquad (2)$$

Chrysotile, Crocidolite and Asbestos Containing Waste (ACW) samples are treated. Chrysotile was the most asbestos variety used for industrials application in France. For this reason, hydrothermal process is applied firstly on this asbestos variety. Then, crocidolite and ACW was respectively denatured. The operational conditions (Temperature, time treatment and mass concentration material/water) of hydrothermal conversion are detailed on (Tableau 1).

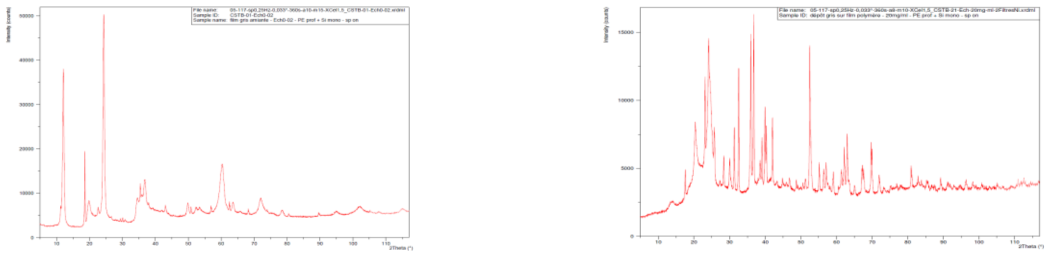
Tableau 1 : MET analyse result for hydrothermal treatment operational conditions

Sample	Temperature (°C)	Pression (MPa)	Time (min)	Material/Water ratio (mg/ml)	META analyse Observation
Chrysotile	400	26	60	0,021	chrysotile
Chrysotile	500	26	60	0,022	chrysotile
Chrysotile	750	28*	10	0,023	chrysotile
Chrysotile	750	18*	30	0,022	chrysotile
Chrysotile	750	27	60	0,022	chrysotile
Chrysotile	750	27	180	0,020	chrysotile desappearance
Chrysotile	750	26	360	0,021	chrysotile desappearance
Crocidolite	750	26	60	0,023	crocidolite
Crocidolite	750	24	180	0,020	crocidolite desappearance
Crocidolite	750	26	360	0,020	crocidolite desappearance
ACW	740	26	360	20	chrysotile desappearance
ACW	740	23	360	170	chrysotile desappearance

*High pressure

The META analyse result (Tableau 1) for all treatment conditions show a chrysotile and crocidolite disappearance after 1 and 3 hour of thermal treatment, for a temperature of T=750°C, a ratio =0.02 mg/ml and pressure of 26 MPa. ACW is transformed in a non-asbestos material, at T=740°C, and t=6h for two mass concentration. Also, for low temperature T≤500°C, chrysotile crystalline structure always persists, despite supercritical environment. Probably, activation energy is not yet reached to initiate structural transformation.

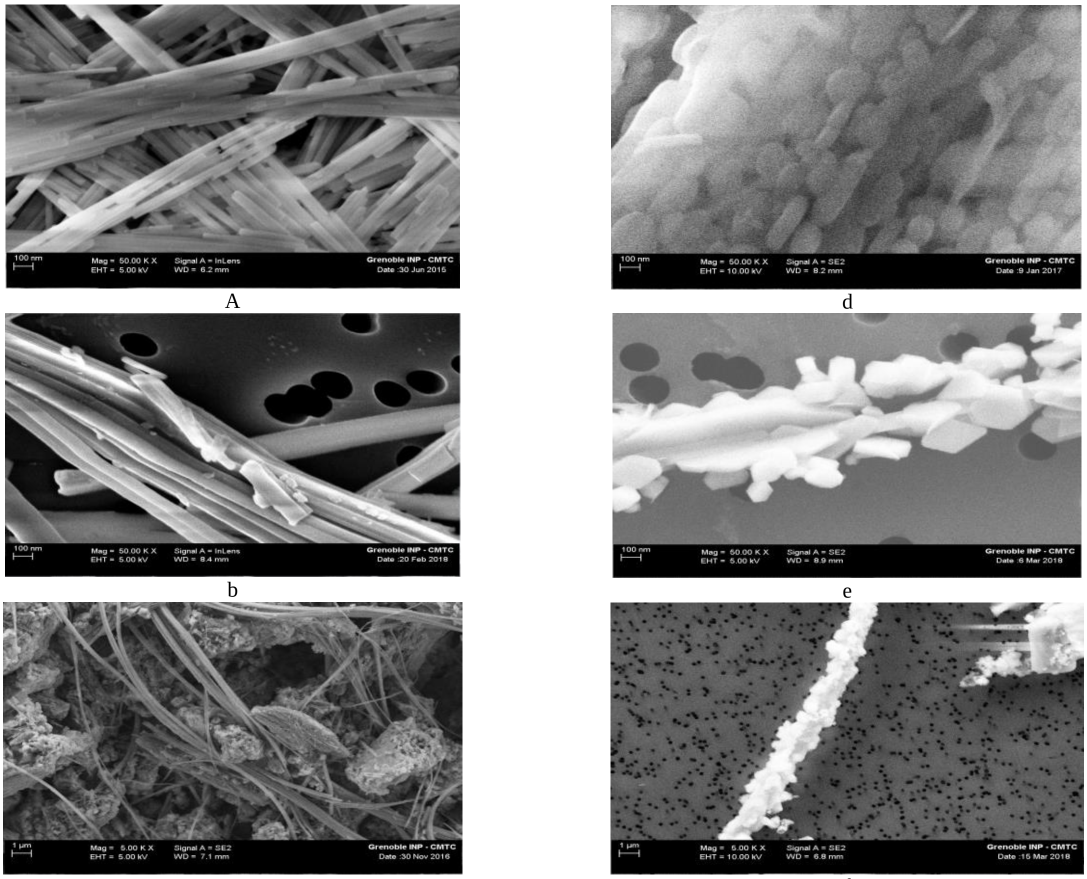
Also, after hydrothermal treatment chrysotile and crocidolite present a fragmented appearance (**Erreur ! Source du renvoi introuvable.**). Nevertheless, in low magnification (X1000), fibrous skeleton still remains.



a b

Figure 2 : XRD spectrum of Chrysotile before (A) and after (B) hydrothermal treatment

A total conversion of chrysotile in forsterite and enstatite is observed in (**Erreur ! Source du renvoi introuvable.**). The XRD spectrum of pure chrysotile present two characteristic peaks [18], respectively (2Ɵ=12,1° and 2Ɵ=24,4°). However, after hydrothermal treatment, these peaks have not been detected in spectrum XRD.



A d

b e

c f

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

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. An ultrasonication post-treatment will be realized to fragment these elongated structure. Finely, an industrial scale hydrothermal energy assessment will give an indication on energy consumption.

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