A study on available technologies to treat asbestos

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Abstract

Asbestos containing waste (ACW) are currently landfilled in specific sites or encapsulated with resins. However, health issues has been highlighted, related to the release of fibres. This has recently resulted in a change of the European approach to this waste. As a consequence, the destruction of asbestos fibres is now regarded as a preferable option compared to landfilling or encapsulation. In this framework, a review of asbestos inertsation technology was performed and data obtained are presented in this document. The review includes thermal (including microwaves and oxyhydrogen), chemical (including hydrothermal and self-propagating chain reactions) and mechanochemical (high energy milling) processes. Each technology is described and compared in terms of efficiency, energy consumption and final use of byproducts.

Keywords

Asbestos-containing materials (ACM), Microwave, Supercritical water

1. Introduction

Asbestos fibres were widely used throughout the world because of their excellent physical properties such as the great tensile strength, poor heat conduction, non-biodegradability, high electrical and alkali and acid attacks resistance and sound absorption capabilities [1]. Because of such properties, asbestos has been widely used particularly as a building and insulation material acoustic and thermal sprays, plasters, paints, flooring products, in flat sheets, tiles, corrugated sheets for roofing, rainwater and pressure pipes and several other building materials. The asbestos contents varied from 25% by weight to over 90% to form a low-cost and easy-to-process material for repairing roofs, forming joints around chimneys, dormer windows, skylights, scuppers, shingles, and nail holes. The composite material was used in a host of applications starting in 1905, its production was increased from approximately 1930–1970 when it plateaued, and remained relatively constant for the next 20 years (from 1970 to 1990) [1].
First evidences of asbestos detrimental effect grew in the '60s so much so demonstrations were made in following years. In fact, asbestos has been classified by the International Agency for Research on Cancer as carcinogen for humans [2, 3]. Then main problem was to dismiss companies, make places safer and healthier and dispose of asbestos.
Once an asbestos product loses its characteristics, or has been abandoned it is deemed asbestos-containing waste. According to current legislation, ACW must be removed and properly managed in accordance with safety regulations.

Considering that removal is the most widely used technique, the question arises of the subsequent handling of ACW. Landfilling is the most widely used technique, although it is not a definitive solution to the problem. Moreover, the European Parliament highlighted the risk that leachate can contain acid-corrosive agents that can partially dissolve the fibres and redistribute them into the environment: in this regard, the European Parliament resolution 2012/2065 (INI) of 14 March 2013 ("asbestos related occupational health threats and prospects for abolishing all existing asbestos") states that: "whereas delivering asbestos waste to landfills would not appear to be the safest way of definitively eliminating the release of asbestos fibres into the environment (particularly into air and groundwater) and whereas therefore it would be far preferable to opt for asbestos inertization plants".

Treatments performed on the ACW following the removal phase can be divided into two categories based on the effect on the material:

- Stabilization (i.e., treatments aimed at reducing the release of fibres)
- Inertization (i.e., treatments that involve a total crystalchemical transformation of the fibres).

With regard to the first category, there is a reduction of the danger of the material, without affecting the modification of the crystalline structure or acting partially on it. The treatments of the second category aim to completely modify the crystallochemical structure of asbestos thereby undermining the danger, and they are very interesting from an environmental point of view. The obtained products can in fact be considered as a new raw material and they are therefore destined for recycling, provided that they comply with strict requirements.

In the present study, the current state of the art on ACW inertization technologies is described, including the physical principles on which they are based, the advantages and disadvantages. This survey will only take into account the methods whose efficiency is claimed to be higher than 99.9% of fibres destruction. All the processes considered can be classified into the following three macro-categories: thermal, chemical and mechanochemical treatments.
The study is based on a patent and literature survey performed with the puropose to identify the optimal method to treat ACW. Considered parameters include energy costs and safety, degradation efficiency and consupmption of chemicals. Furthermore, the possibility to use the obtained byproducts were also taken into account.

2. Asbestos inertisation technologies

2.1 Thermal treatments

Thermal treatments consist of the modification of the crystal-chemical structure, which naturally occurs up to or above 1200 °C. The main advantages connected to thermal treatment are: (i) incorporation of large amounts of heavy metal ions which are chemically bonding inside an inorganic amorphous network; (ii) the final process product is inert towards most chemical or biological agents can be disposed in landfills; (iii) flexibility to treat wastes of various type; (iv) consolidated technology; (v) a reduced amount of waste is obtained.
The common critical issues for all thermal treatments are the high energy required to heat a thermally inert material such as asbestos. Other issues are related to the formation of atmospheric pollutants during the heating phases and in this view a particular problematic material is vinyl-asbestos, since the thermal treatment of halogenated polymers can lead to the formation of persistent organic pollutants such as dioxins and polychlorinated biphenyls.
This category is very articulated and it is also the one where the most important industrial experiences are concentrated. There are several subcategories of thermal treatment, which can be classified according to the technology used to heat, the presence of additives and the heat-up processes (recrystallization).

There are several subcategories of thermal treatment, which can be classified according to the technology used to heat, the presence of additives and the heat-up processes (recrystallization). The different licences, maximum process temperature and energy consumption (if available) are summarized in Table 1.

Simple ***vitrification processes*** is the simplest thermal treatment. In this process the product is inert glass material. In general, the critical issue of all thermal treatments is related to the heating mode of the material. Electric and methane furnaces are generally used to achieve the desired temperatures. An alternative, very efficient but very expensive heating method is represented by the INERTAM process (Morcenx, France), which uses a plasma torch (arcdischarge type) for fusing ACW materials. The vitrification processes may or may not include pretreatments of grinding, which have the purpose of decreasing the dimensions, thus fostering the fusion of the treated materials.
Generally, there are also gas abatement systems that reduce pollutant emissions in the atmosphere. For example, VERT (Vitrification and Environmental Recycling Technology Limited) has proposed the McNeill Vitrification Process (MVP), marketed through the Chemical Exchange Directory s.a., with a pilot unit installed in 1996 near Nuremberg (Germany). An important disadvantage of simple vitrification is due to the high costs of disposal of the product, which, although not harmful, has few applications and must often be treated as a waste (not hazardous). However, if you identify a field of use for this material, the cost of the whole process can be considerably reduced.

Otherwise, ***thermal treatments with controlled recrystallization*** allow to obtain a high quality material which can be used for building materials. Other inorganic materials can also be added to improve the quality of the byproduct. The process is the same of “Thermal treatments with controlled recrystallization”, with the only difference that a heating rate control system is applied. Also in this case, the crushing system is optional and can also be not present. In this subcategory of treatments, most of the patents on inoculation of asbestos are concentrated. Typically, the claims of these patents protect both the process and the material obtained. The thermal conversion of asbestos in ceramic materials has been investigated in full details in the last decades [4-6].

In order to improve the properties and possibilities of using the inert material produced, in addition to the controlled recrystallization described in “Thermal treatments with controlled recrystallization”, it is possible to use ***inorganic materials*** such as clay. The process leads the ACW to be mixed with clay and used in the production of expanded clay: at a drying stage at 300 °C with loss of water of constitution, followed by combustion phases at 1000 °C (in the presence of organic substances), partial melting at 1300 °C and subsequent vitrification only of the outer parts of the clay-based granules that do not melt completely due to the low thermal conductivity of the material leaving adequate porosity inside.

As alternative energy carriers is microwaves. ***Microwave air plasma treatment*** is an electrical discharge and uses microwave as energy. The electromagnetic waves present a wavelength between infrared light and radio waves with high frequency. This treatment technique presents several advantages: electrode-less discharge, high gas temperature (about 3000 °C), compact size and small amount of energy need. In fact the energy demand of microwave air plasma can also be 100 times lower than the thermal inertization, with also the melting time 200 time shorter [7]
Furthermore with this process the oxygen is not a limiting factor thanks to the presence of electrode discharge. The atmospheric microwave air plasma treatment method can treat airborne building materials that contain asbestos. Thus, cement and concrete can also be treated due to the high temperature of plasma. The product of microwave treatment is magnesium oxide which contain compounds in the form of solid blocks based on forsterite (Mg_2SiO_4) as the main crystalline part [8]. Several researchers have demonstrated that asbestos fibres can be easily and rapidly decomposed by microwave irradiation.
For instance, ACW were treated with microwaves obtaining forsterite, a harmless magnesium silicate [9]; in particular it was observed amorphous structures with abundant cordierite that can be applied for recycling instead of Mg-rich talc as raw material. Although scientific evidence demonstrates the feasibility of micro-based asbestos inertia, there is no significant use of this technique on an industrial scale.

An alternative strategy for achieving high temperatures near asbestos is the use of a stoichiometric gas mixture of 1:2 oxygen and hydrogen (***oxyhydrogen***) produced by water electrolysis. The reaction between the two components spontaneously triggers at 570 °C and releases an energy of 241.8 kJ per mole of hydrogen. With this technology it is possible to reach the local temperature of 2800 °C. The disadvantage of this methodology is, of course, the low energy efficiency of the process, where electricity is consumed for electrolysis of water to produce the gaseous mixture. This methodology allows to degrade asbestos with efficiency up to 99% [1].

Table 1 Thermal treatments for asbestos containing waste

Process group	Licence	Process	Maximum process temperature (°C)	Energy consumption (kWh/kg)	References
Simple vitrification	Cea	The process consists of a simple vitrification mechanism by means of a cold and direct high-frequency electric induction furnace	1600	1.0	10
	Defi systemes	The process is based on simple vitrification process for casting by a high-frequency electric furnace	1500	n.a.	11
	Inertam	The process uses the so-called “thermal plasma”, consisting of a partially ionized gas, which through an electric arc reaches the temperature of 1000–1200 °C	1200	0,63	12
	Modyam aspireco	The process is based on a dehydration process in a rotating methane oven,and subsequent solidstate chemical recrystallization in the forsterite mineral	650	n.a.	13
	Verultim	The process consists in the granulation of ACWs, packed in plastic bags, before being introduced into the gas melting oven consisting of an incinerator-type static oven.	1400	n.a.	14
Vitrification with controlled recrystallization	Kryas zetadi	The process consists of thermal conversion by ceramization of the ACW using a continuous furnace.	1200-1300	n.a.	4-6, 15
	Asbestex	In the process the material is granulated in a special mill and transferred into suction to a rotary oven where the temperature reaches 1200 °C.	1250	n.a.	16
Thermal (treatment	Cordiam	In the process the ACW, wet ground and then mixed with clay, is loaded onto a carriage that is entered through an	650-1200	n.a.	17

with other inorganic materials)		electronically controlled opening and it is transferred to the roasting oven. In the oven it undergoes a solid-state thermal transformation.			
	Vitrifix	The process consists in storage and mixing of the ACW, glassy granules (or base materials) and the melting base by 20–80% by weight of ACW, 80–20% of glass scraps and 0.5–5% Of melting base, and of a Verrier type electric furnace maintained at a temperature of 1350–1380 °C, where the asbestos fusion occurs.	1000	n.a.	18
	Enel	The process is a simple melting vitrification process through which light coal ash is used to vitrify ACW, with a thermal fusion cycle at temperatures not higher than 1205 °C for 1 h, followed by melt casting in a cooling pool.	n.a.	1.55	19
	Italcementi	The process involves a thermal treatment (from 600 to 800 °C) without prior grinding of the material.	n.a.	0.5-0.8	20
Microwave	Athon	The process consists in previously ground and reduced to minute particles the ACWs and then mixed with a low-melting in a microwave thermal reactor, where they are heated to a temperature between 900 and 1100 °C	1090	n.a.	21
Oxyhydrogen	Oxyhydrogen	The process use of a stoichiometric gas mixture of 1:2 oxygen and hydrogen (oxyhydrogen) produced by water electrolysis. The reaction between the two components spontaneously triggers at 570 °C and releases an energy of 241.8 kJ per mole of hydrogen.	1450-1550	n.a.	1

2.2 Chemical treatments

Chemical treatment consists in treatment of the compounds included in asbestos structure with chemical additives which are added to lower the melting temperature or enhance mineralogical decomposition. The main advantage of this technique is the reduced energy cost as the decomposition happen also at room temperature, however the main drawbacks are the long treatment time and the need of waste liquid treatment.
In general, in order to obtain satisfactory results, it is necessary to operate at temperatures close to 100 °C. The disadvantages of both techniques are related to the costs associated with the consumption of reagents and the subsequent disposal of wastewater.
As it is necessary to hydrolyse the oxygen–silicon bond, the two main strategies include the use of highly basic (or more rarely acidic) pH that degrades the structure of asbestos by producing free silanols. Another widespread approach is the use of hydrofluoric acid to form silicon fluoride (SiF_4).

Chrysotile asbestos fibres decomposition mechanisms were investigated in aqueous solution of fluorosulfonic acid (HSO_3F). The obtained sulfuric acid reacts with $Mg(OH)_2$ layers of chrysotile fibres [22]. Another approach [23] uses fluoride compounds to chemically and physically break down the asbestos structure. The fluorides react with the silicon in the asbestos crystals to destroy them. In another study [24] microwave and chemical treatment were coupled to transform anisotropic fibres into an isotropic fibre and allow the asbestos inertization and its reuse in cement products. Several treatments have been tested, for example oxalic acid as well was proposed [25] for asbestos fibre degradation, In another study ACW was dissolved with phosphoric acid solution [26]. A specific kind of chemical treatment strategy is represented by a biological technique [27]. Finally, it is worthy of being mentioned another chemical technique [28] which allowed to obtain asbestos inertization using high reactive $CHClF_2$- decomposed acidic gas, generated by the decomposition of Freon.

One of chemical treatment is with ***strong basic solutions***. At high pH, silicate compounds can be degraded by means of the hydrolysis of the Si–O bond, driven by the OH^- anion [29]. This phenomenon is used in several methods to treat ACW.

Under alkaline conditions, asbestos is converted into magnesium hydroxide and sodium silicate. Similar reactions can be derived for the other forms of asbestos, and fro the use of other basic reactants such as potassium hydroxide KOH and calcium hydroxide $Ca(OH)_2$.

Similarly to basic solutions, ***strong acidic solutions*** treatment can hydrolyse the Si–O bond, creating free silanol moieties ($R_3Si–OH$).The wasteless-method process [30] is based on digestion, in two stages, of fibrous minerals with a highly concentrated phosphoric acid (H_3PO_4) solution. Chrysotile is converted into magnesium phosphate and orthosilicic acid. This latter compound is indeed more stable than Mg(OH)2 formed in reaction of "Treatments with strong basic solutions". The best results are obtained with an excess of phosphoric acid at 10% and an optimum temperature of 80 °C, while for lower concentrations and temperatures the fibrous phase is still observed. The whole process is conducted at a temperature of 95 °C for about 1 h. [31].

Another typology of ***treatment is with fluoride***. Hydrofluoric acid is known to spontaneously react with several forms of silica derivatives (SiO_2) such as glass, to form gaseous silicon fluoride (SiF_4). Compared to the use of other acids described in the previous section, this reaction is based on a different process: indeed, the driving force is the formation of SiF_4.

A chemical treatment that eliminates the problem of the handling of corrosive/hazardous reagents is the "***hydrothermal treatment***" [32], which involves the use of supercritical water at 250 MPa and 650 °C. Under such conditions, the physical state of the water is that of supercritical fluid. This approach allows to operate at neutral pH. At present, technology is at a prototype level. The main issues related to the process are: particularly high pressures; filtration of the obtained water, need (in some specific applications) to add 6% of hydrogen peroxide.

Treatment with reducing agents is an other chemical treatment. Silicates such as asbestos can be degraded by reaction with a suitable reducing agent. The process requires the addition of a reducing agent such as a metal in its elementary state (which determines the total cost of the process). Other criticalities of these processes are linked to the onset of reaction. The advantage of this approach is that oxidation–reduction reactions are preferred and once started they proceed spontaneously. The process is called self-propagating high temperature syntheses. For example, it has been shown that asbestos degrades with a mixture of ferric oxide and elementary magnesium [33].

The licences, maximum process temperature and chemicals involved are summarized in Table 2Table 1.

Table 2 Chemical treatments for asbestos containing waste

Process group	Licence	Process	Maximum process temperature (°C)	Chemicals involved	References
Strong basic solution	Tresenerie	The process, which lasts 20–30 min, is based on the dissolution of asbestos fibres in a concentrated and aqueous basic solution (> 25 M) of sodium hydroxide (NaOH) or potassium hydroxide (KOH) contained within a reactor at a relatively moderate and variable temperature between 160 and 175 °C, preferably 170 °C, and at a low pressure of between 8 and 10 kg/cm2.	200	NaOH or KOH	34
	Treatment with fly ash	In the process a fly ash solution containing sulfur and calcium hydroxide was used at room temperature in a ball mill.	Room temperature	Fly ash	35
Strong acid	Wasteless method	The wasteless-method process is based on digestion, in two stages, of fibrous minerals with a highly concentrated phosphoric acid (H3PO4) solution.	80	H_3PO_4	30,36
Fluoride	ABCOV	The ACWs are first treated with an aqueous solution consisting of a weak organic acid (selected from trifluoroacetic acid, acetic acid, benzoic acid, p-cyanobenzoic acid, p-trifluoromethyl acid and lactic acid,) and a pH between 3 and 6 and subsequently ground to wet.	80	HF	37-40
Hydrothermal	S-SYSTEM	The process consists of hydro-thermal treatment with supercritical water at a pressure of between 25 and 27 MPa and at	650	H_2O_2	41

		a temperature ranging between 600 and 650 °C.. The method also foreseen the addition to the aqueous phase of an oxidizing compound at a predetermined concentration, such as hydrogen peroxide.			
	Chemical Center	The process combines an acid treatment with a hydrothermal treatment using an acid industrial waste product, i.e., whey of exhausted milk.	250	Milk whey	42
Reducing agents	Self-propagating reactions	The process is called self-propagating high temperature syntheses. For example, it has been shown that asbestos degrades with a mixture of ferric oxide and elementary magnesium.	1600	Mg + Fe_2O_3	33

2.3 Mechanochemical treatments

The mechanochemical treatments rely on the mechanical energy transmitted to the ACW by crushing machines the task of destroying the crystal lattices and the molecular bonds present in asbestos, [43]. High-energy milling or ultramilling processes have been successfully proposed and used at the real and laboratory scale to handle the ACW. Specifically, it has been shown that milling of phyllosilicates, which takes place in mills operating with the most different methodologies, results in the progressive amorphization by the release of the hydroxyl ions needed to maintain the crystalline structure: with this regard, the process is called "cold vitrification". The licence are summarized in Table 3Table 1.

Table 3 mechanochemical treatments for asbestos containing waste

Process group	Licence	Process	References
high-energy milling	HEM	The ACW seals in polyethylene and partially wet bags are opened in a laminar flow hood in order to avoid aerodispersion of the fibres and subsequently under the hood, milled in a mortar and reduced to millimetres. These samples are then transferred to a ball mill. Grinding lasts for about 2 h.	44

3. Conclusions

In this study, several technologies for asbestos inertisation have been reviewed. In order to select a suitable methodology, energy consumption can be regarded as a key factor: with regard to process temperature, there is a strong difference between thermal treatments (both vitrification and microwave) and other treatments (chemical, mechanochemical): as a consequence, thermal treatments are characterized by higher energy consumption. The technology which requires the lowest energy use is the chemical treatment. However, other parameter should be considered: indeed, costs are also related to products input and management of output byproducts: with this regard, chemical treatments have the highest costs in terms of wastewater management and chemical consumption. On the other hand, chemical treatments are also the only treatment category in which emissions in the atmosphere are not present. The several treatment methods can also be compared in terms of final product quality: indeed, some methodologies allow to better exploit the potential use of the inert material, such as thermal treatments with controlled recrystallization. The costs are due to different reasons, such as energy consumption for heat/ microwave generation, chemical products consumption and disposal, etc. As a consequence, each technology presents advantages and disadvantage and can be selected on the base of the specific process needs. In particular, the possibility to obtain a reusable byproduct can be seen as the most important technical point in order to reach the economic feasibility of a plant.

This survey confirms that, in spite of the low industrial development of asbestos treatment plants all over the world, the readiness level of some technologies is nowadays able to tackle the problem of asbestos-containing materials. Indeed, a number of applications is available for a reliable thermal degradation of asbestos. Of course, all techniques are currently very expansive when compared to landfilling: this could be the major reason of the low industrial development for these kinds of technology. The costs are due to different factors, such as energy consumption for heat/ microwave generation, chemical products consumption and disposal, etc. As a consequence, each technology presents advantages and disadvantage and can be selected on the base of the specific process needs. In particular, the possibility to obtain a reusable byproduct can be seen as the most important technical point in order to reach the economic feasibility of a plant. Further details on these technologies are reported in a related paper [45].

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