



(11) **EP 2 428 254 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
27.03.2013 Bulletin 2013/13

(51) Int Cl.:
A62D 3/02 (2007.01) **A62D 3/35** (2007.01)
A62D 3/36 (2007.01)

(21) Application number: **11175285.3**

(22) Date of filing: **26.07.2011**

(54) **Process for treating an asbestos containing material**

Verfahren zur Behandlung von asbesthaltigem Material

Procédé pour traiter un matériau contenant de l'amiante

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME

(30) Priority: **30.07.2010 IT MI20101443**

(43) Date of publication of application:
14.03.2012 Bulletin 2012/11

(73) Proprietor: **Chemical Center S.r.l.**
40050 Castello d'Argile (BO) (IT)

(72) Inventors:
• **Balducci, Giulia**
47921 RIMINI (IT)
• **Foresti, Elisabetta**
55045 PIETRASANTA (LUCCA) (IT)
• **Lelli, Marco**
40063 MONGHIDORO (BOLOGNA) (IT)
• **Lesci, Isidoro Giorgio**
48014 CASTEL BOLOGNESE (RAVENNA) (IT)
• **Marchetti, Marco**
**63062 MONTEFIORE DELL'ASO (ASCOLI
PICENO) (IT)**

• **Pierini, Filippo**
61037 MONDOLFO (PESARO-URBINO) (IT)
• **Roveri, Norberto**
40133 BOLOGNA (IT)

(74) Representative: **Biggi, Cristina**
Bugnion S.p.A.
Viale Lancetti 17
20158 Milano (IT)

(56) References cited:
• **STANIK INGA ADAMINA ET AL: "Destruction of
the chrysotile asbestos structure with a
population of the bacteria Lactobacillus casei
and Lactobacillus plantarum", FRESENIUS
ENVIRONMENTAL BULLETIN, FREISING-
WEIHENSTEPHAN, DE, vol. 15, no. 7, 1 January
2006 (2006-01-01), pages 640-643, XP008134671,
ISSN: 1018-4619**
• **DATABASE WPI Week 200728 Thomson
Scientific, London, GB; AN 2007-292346
XP002630201, & WO 2007/032412 A1 (INST ECO
& ECONOMY SYSTEM CORP) 22 March 2007
(2007-03-22)**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 2 428 254 B1

Description

[0001] The present invention relates to a process for treating an asbestos containing material so as to transform the asbestos itself and enable a possible reuse of the products deriving from said treatment.

[0002] Asbestos is the commercial name attributed to several natural minerals having a fibrous structure and belonging to the class of silicates. In modern times some of these minerals were widely used because of their excellent technological properties: they have good resistance to heat and fire, to the action of chemical and biological agents and to abrasion and wear, have high mechanical strength and good flexibility, easily bind with construction materials and have good sound absorbing and heat insulating properties. Because of all these properties and its low cost asbestos was widely used in industrial and building applications and manufactured components, in means of transport and in the domestic sphere. In particular, the raw fibre was processed in order to obtain various products adaptable to multiple uses. In these products, the asbestos fibres may either be free, or strongly or weakly bound. If they are weakly bound, they are referred to as brittle materials, which can be crumbled by hand pressure alone due to the poor internal cohesion. If they are strongly bound, they are referred to as compact materials, which can be crumbled into powder only with the aid of mechanical machinery. The materials in a brittle matrix are undoubtedly the most dangerous, as the fibres can be dispersed into the air with extreme ease and thus inhaled. Asbestos in a compact matrix, given its nature, does not tend to release fibres and a hazardous situation may arise only if it is abraded, deteriorated or sawed.

[0003] There are a vast number of types of Asbestos Containing Materials (ACM) which have extremely varied and differentiated characteristics and uses. The U.S. Federal Register lists over 3000 finished objects which contain asbestos. ACM can be classified into three categories

(a) Surface Materials: these include ACM sprayed or distributed by spreading over surfaces (weight-bearing elements, walls, ceilings) for soundproofing, heat insulating and decorative purposes;

(b) Heat Insulation Materials: these include the ACM used to prevent the formation of condensate in pipes, ducts, boilers, tanks and in various components of water cooling systems, as well as in heating, ventilation and air conditioning systems;

(c) Sundry Materials: this category embraces all of the other ACM, as in false-ceilings, sheathing, fabrics, etc.

[0004] Asbestos has been undoubtedly most widely used in the building sector, in particular in the form of a composite of asbestos and cement, or so-called asbestos-cement. Moreover, in order to avoid or limit damage in the event of a fire, asbestos was largely used as a coating on beams or floors, applied with spraying and spreading techniques. The heat-resistant mixture was composed of varying percentages of asbestos and other materials (vermiculite, sand or cellulose fibres) and binding materials (gypsum and/or calcium carbonate): the result was a continuous layer, soft to the touch, of a colour varying from dark grey to white. Asbestos minerals were used as additives in cement conglomerates to improve their mechanical characteristics: the phases were usually Portland cement, water, aggregates, fibres of Chrysotile, Crocidolite and/or Amosite (more rarely), until eventually only Chrysotile was used. The asbestos content was variable and could reach 50% by weight depending on the type of product to be obtained.

[0005] Today it is a universally recognized fact that asbestos is one of the materials most hazardous to human health among those present in living and work environments; this hazard results in severe pathologies prevalently affecting the respiratory tract. Although an etiological connection between the inhalation of airborne asbestos fibres and the onset of specific diseases was already hypothesized at the start of the last century, it was not until the 1990s that regulations consistent with the hazardousness of the material were introduced in various countries.

[0006] Ascertainment of the harm that this raw material caused to workers obliged the governments of all countries in the world to address the problem, in consideration of the exceedingly high social costs ensuing from occupational diseases developed by operators in the sector over the years.

[0007] It should be noted that the accumulation of Asbestos Containing Waste (ACW) in landfills does not solve the problem, but rather simply passes it on to future generations: it is thus important to devise a strategy that allows ACW to be transformed and subsequently exploited as materials in the production of new products which are totally safe from an environmental viewpoint.

[0008] There are currently in use a number of processes, in addition to ACW "inertization" and "isolation", which are suitable for transforming it and have the aim of completely eliminating the hazardousness thereof. "Inertization" processes comprise procedures for conditioning in matrices of varying nature which prevent the dispersal of asbestos fibres in the environment, whereas "transformation" processes act directly upon the fibrous structure of the mineral itself, transforming it into other phases that are not hazardous to human health.

[0009] The main ACW transformation processes are based on chemical treatments relying on the action of acids and thermal and mechanochemical treatments, though recently biochemical and microbiological methods have been studied.

[0010] Insofar as regards acid treatments, various methods have been developed which envisage the use of both organic and mineral acids to transform ACW so as to obtain secondary materials that are recyclable and often reusable

in the ceramics industry. In particular, the effects of mineral acids, such as hydrofluoric, hydrochloric and sulphuric acid, as well as the effects of organic acids such as formic and oxalic acid, have been studied.

[0011] As regards thermal treatments, it is well known that asbestos materials are unstable at high temperatures. Chrysotile, for example, has a tendency to lose the hydroxyl groups at 500-600°C and to be transformed into a different inert mineral phase, Forsterite, which is recrystallized at 820°C. The application of this principle makes it possible to obtain inert materials from ACW, as such or ground, and treated in furnaces at a temperature of 800-950°C. Furthermore, if heating is preceded by compacting of the material, the consequent disorientation of the crystals allows the final product to be used as electrical insulation or refractory material. This process takes the name of ceramization. It is also possible to achieve a vitrification of ACW through a number of processes which are based on melting asbestos containing waste with the addition of different additives within a broad temperature interval (1300-1800°C), followed by rapid cooling with the production of an inert material having an amorphous vitreous structure. However, this solution requires a great deal of energy in order to bring the melting ovens to extremely high, constant temperatures.

[0012] In vitroceramization, on the other hand, the waste is melted at temperatures of between 1300 and 1400°C together with particular additives, such as blast furnace slag or industrial sludge, forming a mixture with a high metal content. The slag thus derived is crystallized at a controlled temperature: in this manner one obtains products with very high mechanical strength, particularly suitable as coating and protective surfaces in the building, mechanical and chemical industries.

[0013] Another technique consists in the so-called lithification, which is based on melting ACW derived from the removal of insulation from railway carriages at a temperature of 1300-1400°C. Slow cooling brings about the crystallization of pyroxenes, olivine and iron oxides. The final result of the treatment is the production of inert materials, which can be recovered for a variety of applications.

[0014] As regards biological treatments, the microbiological action of mosses and lichens on different rocky substrates containing asbestos fibres has been studied both in vivo and in vitro: the hyphae of lichens and fungi are capable of penetrating and secreting chemical compounds (oxalic acid is one of the primary metabolites), some of which can alter the mineralogical structure of asbestos fibres (see for example the article by S.E. Favero-Longo, M. Girlanda, R. Honnegger, B. Fubini, R. Piervittori; Mycological Research, Vol. 111, Issue 4, pp. 473-481 (2007)).

[0015] Microbiological methods have also been developed for the transformation of asbestos using bacteria, in particular *Lactobacillus casei* and *Lactobacillus plantarum* (see for example the article by I.A. Stanik, K. Cedzynska, S. Żkowska; Fresenius Environmental Bulletin, Vol. 15, Issue 7, pp.640-643 (2006)). The method is based on breaking down the crystalline layers of Brucite (magnesium-oxygen) present within the crystalline layers of Chrysotile as a consequence of the indirect metabolism of the bacterial cultures used. The decomposition of crystalline layers seems to be due to the acidification of the reaction environment, thanks to the presence of metabolites secreted by the bacteria, which also include lactic acid. The hypothesized reaction mechanism is achieved through a substitution of Mg^{2+} ions by H^+ ions, which are present in great excess. The magnesium thus released reacts with the lactic acid present to form soluble salts.

[0016] However, all the processes that use biochemical and microbiological methods have shown a low degree of asbestos fibre transformation, at times only superficial, without reaching a complete transformation: therefore, up to now such methods have not had applications feasible on an industrial scale.

[0017] Unfortunately, the methods for transforming asbestos containing materials (ACM) known to date have non-negligible disadvantages. In particular, acid treatments lead to the accumulation of a large amount of waste products, which also need to be disposed of. Furthermore, it should be kept in mind that in order to treat millions of tons of ACW (the approximate estimate for Italian territory alone ranges between 20 and 30 million tons) it would be necessary to use enormous amounts of reagents, which would entail non-negligible environmental risks and very high costs. With regard to thermal treatments, the largest disadvantage, besides the enormous amount of energy required to bring the furnaces to very high, constant temperatures, is given by the fact that suitable equipment is highly costly and thus scarcely available across the territory, so that it is necessary to transport the ACW over long distances, with the consequent environmental risks and logistical costs.

[0018] The Applicant thus addressed the problem of devising and fine-tuning a process for treating asbestos containing materials under relatively mild conditions, which is able to combine efficacy with both ecological and economic sustainability.

[0019] The Applicant therefore judged it expedient to couple a thermal treatment to an acid treatment in which the asbestos containing material in a broken-down form is subjected to the action not of a common acidic chemical reagent, but rather of an acidic industrial waste product, i.e. milk whey, which, besides creating an acidic environment, contributes bacterial components believed to favour an attack on the material itself. After said treatment, which frees the asbestos fibrils from the matrix in which they are englobed, the asbestos is then inertized by means of a high-temperature, high-pressure hydrothermal process. At the end of this process one obtains a solid phase consisting essentially of silicates and oxalates together with an organic component resulting from the thermal transformation of the bacterial component, and a liquid phase that is rich in various metal ions (in particular magnesium, nickel, manganese, potassium and calcium),

which can be recovered through electrolytic processes.

[0020] The present invention thus relates to a process for treating an asbestos containing material, comprising:

treating the material with milk whey so as to obtain an acidic liquid phase and a solid phase containing the asbestos;
subjecting the solid phase containing the asbestos to a hydrothermal process at a temperature of from 120°C to 250°C and at a pressure of from 5 bar to 20 bar.

[0021] In a preferred embodiment, the milk whey is preferably exhausted milk whey.

[0022] In a preferred embodiment, the hydrothermal process is carried out at a pH value of from 1 to 7, more preferably from 2 to 6.

[0023] As regards the asbestos containing material, it can be any product which includes asbestos in a fibrillar form, in brittle matrices or a cement matrix, or also compact polymeric matrices (generally synthetic or cellulosic polymers). If asbestos containing materials are used in compact non-cement matrices, a pre-treatment of the material which is capable of freeing the fibres from the matrix itself is preferably carried out, as is better illustrated below.

[0024] For example, the asbestos containing material can be:

(a) a material for covering surfaces for the purpose of imparting sound-absorbing, heat-insulating, flameproofing and/or decorative properties, in which the asbestos fibres are mixed with inorganic components (e.g. silicates, gypsum and/or calcium carbonate) and applied by spraying or spreading (for example to obtain flameproof barriers in ducting for electrical installations, or for insulating railway carriages, ships and buses);

(b) a material in the form of ropes, tapes or sheaths obtained by weaving asbestos fibres, generally in a blend with other natural and synthetic fibres, and usable for wrapping pipes to be heat insulated or electric cables near sources of intense heat, or for producing fireproof fabrics or fabrics with properties of resistance to the corrosive action of acids and bases.

(c) a material in which the asbestos fibres are contained in a cellulose-based matrix, which can be pressed to obtain sheets to be used, for example, as flameproof barriers or as coverings for bearing surfaces, sleeves or panels of compressed raw fibres, used to insulate pipes for conveying high-temperature steam, or as industrial filters;

(d) a material obtained by blending asbestos with cement (known as asbestos-cement), in which the asbestos is present in a variable amount of up to 50% by weight, in general between 15 and 20% by weight, relative to the total weight of the material, for the manufacture of building components (e.g. tiles, partitions, pipes, roofing elements, tanks, flat or corrugated sheets, etc.).

[0025] The aforesaid asbestos containing materials are generally delivered as waste to be disposed of, and in order to transport them safely they are preferably wrapped with a protective film, which is preferably made from a biodegradable polymer (e.g. starch derivatives, polylactic acid, polyhydroxyalkanoates).

[0026] To avoid the volatilization of the asbestos fibres, the material to be treated is preferably kept wrapped in said film also during the grinding process, which is carried out in order to obtain said material in a broken-down form. Grinding has the purpose of obtaining fragments of a size which can vary within wide margins, such as to render the material itself compatible with the specific equipment used for the subsequent steps and to increase the exchange surface and thereby reduce treatment times. The size can therefore vary from micrometric dimensions to several centimetres, for example between 1 and 5 cm. The grinding process can be carried out with various types of machinery, depending on the specific material to be treated.

[0027] In a preferred embodiment, the grinding step is carried out on the material immersed in a tank containing the milk whey. This prevents the asbestos fibres from being dispersed in the environment during grinding. Said grinding can preferably be achieved by means of diamond cutters, which are capable of working immersed in the milk whey.

[0028] If the material to be treated comprises asbestos in a fibrillar form dispersed in a compact polymeric matrix (generally synthetic or cellulosic polymers, e.g. paper or cardboard), prior to the treatment with milk whey the asbestos containing material is preferably subjected to a thermal pre-treatment in order to cause combustion of the polymeric matrix and to release the asbestos fibrils.

[0029] As regards milk whey, as is known, the latter consists in the liquid part which separates from the curd as a result of the process of coagulation of the casein present in the milk. It is thus a by-product of the production of cheese or casein from milk. Whey can be considered as the aqueous phase of milk. This phase is formed by the whole of the substances dissolved in the water (including soluble proteins), irrespective of their molecular size, and by substances with low molecular weights. The composition of milk whey is highly complex and mainly comprises water, lactose, protein, fats and vitamins. Thanks to the presence of large amounts of protein and other nutritionally valid compounds, milk whey is further used in various ways, in particular for the production of cheese and other milk derivatives. The waste liquid phase which derives from this second processing is the so-called "exhausted milk whey", which is considered non-hazardous special waste. In the following table a typical composition of exhausted milk whey is shown:

Substances Present	Average Amount (% by weight)
Lactose	4.0 ÷ 4.6
Protein	0.10 ÷ 0.15
Fats	0.15 ÷ 0.30
Salts	0.9 ÷ 1.1
Organic acids	0.20 ÷ 0.25
pH	3.5 ÷ 5.2

[0030] It should be noted that exhausted milk whey can have a variable composition depending on the specific manufacturing processes carried out in the dairy, which differ from product to product and also show seasonal variability.

[0031] It is worth highlighting that exhausted milk whey, despite being wholly devoid of toxic agents, cannot be disposed of directly in bodies of water due to its high organic content and the presence of complex bacterial flora. For the same reason, treating it by means of classic biological purification systems is exceedingly difficult and costly. A particularly innovative and economically relevant aspect of the present invention is precisely that it provides a process which not only allows asbestos containing waste to be treated so as to render it no longer hazardous to health, but also enables the disposal of huge amounts of milk whey, and in particular exhausted milk whey, which represents a serious ecological problem for the dairy industry.

[0032] Thanks to the acidity of milk whey, and in particular of exhausted milk whey, which generally has pH values from 3.5 to 5.5, and the concomitant presence of bacteria (in particular *Lactobacilli*), the cement matrix in which the asbestos may be englobed in the form of fibrils is gradually transformed, with the production of carbon dioxide, so as to release the asbestos fibrils, which remain suspended in the liquid inside the tank where the treatment is carried out.

[0033] If the pH of the milk whey is not sufficiently acidic for an optimal execution of the process, at least one organic acid can be added to the milk whey, in particular lactic acid or oxalic acid, so as to bring the pH to a value of between 1 and 3.

[0034] Preferably, the amount of milk whey used in the process according to the present invention can vary from 2 to 100 times by weight, preferably from 20 to 40, relative to the weight of the total material to be treated. The treatment with milk whey is carried out under stirring for a time of from 12 to 120 hours, more preferably from 48 to 72 hours, at a temperature of from 20 to 90°C, more preferably from 30 to 50°C.

[0035] During the treatment of ACM in a brittle or cement matrix with exhausted milk whey, carbon dioxide is formed as a result of the action of the acidic environment on the carbonates present in the cement. This step of the process is preferably carried out in a closed tank, so that the carbon dioxide formed can be collected and conveyed into a plant where it is used without being emitted into the atmosphere: for example, a plant for the production of natural gas or biogas or for the production of biopolymers (e.g. polyhydroxyalkanoates) using specific cell cultures.

[0036] At the end of the treatment with milk whey, the solid phase containing the asbestos is conveyed, for example by suction, into a hydrothermal reactor (preferably made of steel) where the hydrothermal treatment is carried out at a temperature of from 120°C to 250°C, preferably from 160°C to 200°C, and at a pressure of from 5 to 20 bar, preferably from 8 to 15 bar.

[0037] As indicated above, the hydrothermal process is preferably carried out at a pH value of from 1 to 7, more preferably from 2 to 6. If the pH of the solid phase is not sufficiently acidic for an optimal execution of the process, it is possible to add at least one organic acid, in particular lactic acid or oxalic acid, to the reaction medium so as to bring the pH to the desired value.

[0038] As regards the hydrothermal treatment times, the Applicant has found that excessively prolonging this step may lead to an unexpected increase in the concentration of asbestos fibres. This is attributable to the formation of Chrysotile crystals, mainly during the prolonged stages of the process and this to an insufficient transformation. To prevent the crystallization of fibrous Chrysotile during the hydrothermal process it is preferable to add at least one aluminium and/or iron salt to the reaction bath. It is believed that such salts are able to favour, in the event of recrystallization of the asbestos during the treatment, the formation of lizardite and/or antigorite instead of the unwanted Chrysotile phase.

[0039] The hydrothermal treatment is preferably carried out for a time of from 12 to 168 hours, preferably from 72 to 100 hours, and preferably no longer than 120 hours.

[0040] Since the hydrothermal process takes place in the presence of water, the asbestos containing solid phase deriving from the first step of the process generally has water or, preferably, milk whey added to it, the latter being able to contribute the necessary amount of water.

[0041] In order to favour the phase transition from asbestos to nontoxic inorganic compounds, during the hydrothermal

treatment it is advisable to add at least one chelating agent, selected for instance from among: oxalic acid, lactic acid, formic acid, or salts thereof.

[0042] The chelation of magnesium ions is believed to promote cleavage of the Chrysotile crystal planes. Once the structural order characterizing it has been broken down, the asbestos (and in particular Chrysotile) will no longer be capable of packing according to its distinctive basic structural units and undergo a phase change.

[0043] Using at least one chelating agent in this step could also be useful for extracting some important constituent and substituent elements of asbestos, such as, for example, magnesium, nickel and iron, which can be recovered, for example, by means of electrochemical processes.

[0044] As illustrated above, the process according to the present invention leads to the obtainment of different by-products, which can be individually used for a variety of purposes. In particular, the following are obtained:

1) an inorganic solid phase deriving from the hydrothermal treatment, which mainly comprises oxalates, carbonates and silicates and is usable as a starting material for the ceramics industry and inorganic inert matrices;

2) an organic solid phase deriving from the hydrothermal treatment, consisting mainly of thermally treated bacterial residues and usable as an agricultural fertilizer with a high nitrogen content;

3) a liquid phase deriving from the hydrothermal treatment, consisting in an aqueous solution of metal ions, particularly rich in magnesium, nickel, manganese, potassium, iron and calcium, from which the various elemental metals can be electrolytically extracted at a high degree of purity and with substantial financial advantages;

4) a gaseous phase deriving from the treatment of the asbestos containing material with the exhausted milk whey, mainly consisting in CO₂, which can be used, for example, by employing specific bacterial strains, to generate natural gas or biogas (which can satisfy, at least in part, the energy needs of the asbestos containing material treatment plant) and polymeric material having a high technological value.

[0045] The present invention will now be further illustrated with some examples of embodiments, which are provided for purely illustrative purposes without limiting the scope of the invention itself.

EXAMPLE 1

[0046] 4 g of a previously ground asbestos-cement sample was weighed. This was added to 90 mL of exhausted milk whey at pH 4.16.

[0047] The mixture was kept under stirring at a temperature of 30°C for an overall time of 80 hours. At the end of this treatment the pH was 5.82.

[0048] The resulting solid phase, after undergoing filtration, was placed in a hydrothermal reactor together with 60 mL of exhausted milk whey, at a temperature of 150°C and a pressure of between 7 and 9 bar for 72 hours.

[0049] At the end of this second step the resulting sample contained some constituent elements of the cement matrix (calcium carbonate, quartz and anorthite), whereas the percentage by weight of asbestos fibres decreased considerably, from 12% in the untreated sample to 2% in the solid residue at the end of the treatment.

EXAMPLE 2

[0050] 3.5 g of a previously ground asbestos-cement sample was weighed. This was added to 80 mL of exhausted milk whey, to which 10 mL of 0.5 M lactic acid was added. The resulting pH was 3.56.

[0051] The mixture was kept under stirring at room temperature for an overall time of 60 hours. At the end of this treatment the pH was 5.12.

[0052] The resulting solid phase, after undergoing filtration, was placed in a hydrothermal reactor together with 50 mL of exhausted milk whey, at a temperature of 190°C and a pressure of between 8 and 12 bar for 60 hours.

[0053] At the end of this second step the resulting sample contained some constituent elements of the cement matrix (calcium carbonate, quartz and anorthite), whereas the percentage by weight of asbestos fibres decreased considerably, from 12% in the untreated sample to 5% in the solid residue at the end of the treatment.

EXAMPLE 3

[0054] 4 g of a previously ground asbestos-cement sample was weighed. This was added to 70 mL of exhausted milk whey, to which 10 mL of 0.5 M oxalic acid was added. The resulting pH was 2.38.

[0055] The mixture was kept under stirring at a temperature of 40°C for an overall time of 48 hours. At the end of this treatment the pH was 6.45.

[0056] The resulting solid phase, after undergoing filtration, was placed in a hydrothermal reactor together with 70 mL of exhausted milk whey, at a temperature of 200°C and a pressure of between 15 and 20 bar for 72 hours.

[0057] At the end of this second step, a complete transformation of the cement matrix was noted, with the exception of a slight percentage of quartz. The percentage by weight of asbestos fibres decreased considerably, from 12% in the untreated sample to 2.5% at the end of the treatment.

EXAMPLE 4

[0058] 3 g of a sample containing free asbestos fibres was weighed; these were quantified in an interval of from 10 to 14% by weight. The sample was added to 50 mL of exhausted milk whey at pH = 3.98 and subjected to a hydrothermal treatment at a temperature of 150°C and a pressure of between 6 and 8 bar for 48 hours.

[0059] At the end of this treatment the percentage by weight of the asbestos fibres had decreased to 2.5%.

EXAMPLE 5

[0060] 4 g of a sample containing free asbestos fibres was weighed; these were quantified in an interval of from 10 to 14% by weight. The sample was added to 60 mL of exhausted milk whey and 10 mL of 0.5 M lactic acid for a pH value equal to 3.56. The sample was subsequently subjected to a hydrothermal treatment at a temperature of 180°C and a pressure of between 8 and 12 bar for 60 hours.

[0061] At the end of this treatment the percentage by weight of the asbestos fibres had decreased to 4%.

EXAMPLE 6

[0062] 4 g of a sample containing free asbestos fibres was weighed; these were quantified in an interval of from 10 to 14% by weight. The sample was added to 70 mL of exhausted milk whey and 10 mL of 0.5 M oxalic acid for a pH value equal to 2.19. The sample was subsequently subjected to a hydrothermal treatment at a temperature of 150°C and a pressure of between 6 and 8 bar for 72 hours.

[0063] At the end of this treatment the percentage by weight of the asbestos fibres had decreased to 2.5%.

Claims

1. Process for treating an asbestos containing material, comprising:

treating the material with a milk whey so as to obtain an acidic liquid phase and a solid phase containing the asbestos;

subjecting the solid phase containing the asbestos to a hydrothermal process at a temperature of from 120°C to 250°C and at a pressure of from 5 bar to 20 bar.

2. Process according to claim 1, wherein the milk whey is exhausted milk whey.

3. Process according to any one of the preceding claims, wherein the hydrothermal process is carried out at a pH value of from 1 to 7, preferably from 2 to 6.

4. Process according to anyone of the preceding claims, wherein the asbestos containing material includes asbestos in a fibrillar form dispersed into a brittle matrix or a cement matrix, or alternatively in a polymeric compact matrix.

5. Process according to anyone of the preceding claims, wherein the asbestos containing material includes asbestos in a fibrillar form dispersed into a polymeric compact matrix, and wherein said material, before the treatment step with the milk whey, is subjected to a thermal pre-treatment to cause combustion of the polymeric matrix and to release the asbestos fibrils.

6. Process according to anyone of the preceding claims, wherein the asbestos containing material is previously subjected to a grinding step.

7. Process according to claim 6, wherein the grinding step is carried out on the material immersed into a tank containing the milk whey.

8. Process according to anyone of the preceding claims, wherein the milk whey is added with at least one organic acid, particularly lactic acid or oxalic acid, so as to obtain a pH value of from 1 to 3.

9. Process according to anyone of the preceding claims, wherein the milk whey is employed in an amount of from 2 to 100, preferably from 20 to 40, times by weight relative to the weight of the material to be treated.
- 5 10. Process according to anyone of the preceding claims, wherein the treatment with the milk whey is carried out under stirring for a time of from 12 to 120 hours, preferably from 48 to 72 hours, at a temperature of from 20 to 90°C, preferably from 30 to 50°C.
- 10 11. Process according to anyone of the preceding claims, wherein the hydrothermal process is carried out at a temperature of from 160°C to 200°C and at a pressure of from 8 to 15 bar.
12. Process according to anyone of the preceding claims, wherein the hydrothermal process is carried out for a time of from 12 to 168 ore, preferably from 72 to 100 hours, and more preferably not longer than 120 hours.
- 15 13. Process according to anyone of the preceding claims, wherein, before the hydrothermal process, water or, preferably, milk whey is added to the solid phase containing the asbestos.
14. Process according to anyone of the preceding claims, wherein, during the hydrothermal process, at least one chelating agent is added, selected for instance from: oxalic acid, lactic acid, formic acid, or salts thereof.

Patentansprüche

1. Verfahren zur Behandlung von asbesthaltigem Material, umfassend:

25 Behandlung des Materials mit einer Molke, um eine saure Flüssigkeitsphase und asbesthaltige Festphase zu erhalten;
 Aussetzen der asbesthaltigen Festphase einem hydrothermischen Verfahren bei einer Temperatur von 120 °C bis 250 °C und bei einem Druck von 5 bar bis 20 bar.

- 30 2. Verfahren nach Anspruch 1, wobei die Molke exhaustierte Molke ist.
3. Verfahren nach einem der vorangehenden Ansprüche, wobei das hydrothermische Verfahren bei einem pH-Wert von 1 bis 7, vorzugsweise von 2 bis 6 durchgeführt wird.
- 35 4. Verfahren nach einem der vorangehenden Ansprüche, wobei das asbesthaltige Material Asbest in fibrillärer Form, dispergiert in eine spröde Matrix oder eine Zementmatrix, oder alternativ in eine kompakte Polymermatrix umfasst.
5. Verfahren nach einem der vorangehenden Ansprüche, wobei das asbesthaltige Material Asbest in fibrillärer Form, dispergiert in eine kompakte Polymermatrix, umfasst und wobei das Material vor dem Behandlungsschritt mit der Molke einer thermischen Vorbehandlung unterzogen wird, um die Verbrennung der Polymermatrix zu verursachen und die Asbestfibrillen freizugeben.
- 40 6. Verfahren nach einem der vorangehenden Ansprüche, wobei das asbesthaltige Material zuvor einem Mahlschritt unterzogen wird.
- 45 7. Verfahren nach Anspruch 6, wobei der Mahlschritt mit dem Material durchgeführt wird, das in einen die Molke enthaltenden Behälter eingetaucht ist.
8. Verfahren nach einem der vorangehenden Ansprüche, wobei der Molke mindestens eine organische Säure zugesetzt wird, im Besonderen Milchsäure oder Oxalsäure, um einen pH-Wert von 1 bis 3 zu erhalten.
- 50 9. Verfahren nach einem der vorangehenden Ansprüche, wobei die Molke in einer Menge von 2 bis 100 eingesetzt wird, vorzugsweise von 20 bis 40, mal Gewicht relativ zum Gewicht des zu behandelnden Materials.
- 55 10. Verfahren nach einem der vorangehenden Ansprüche, wobei die Behandlung mit der Molke unter Rühren für einen Zeitraum von 12 bis 120 Stunden durchgeführt wird, vorzugsweise von 48 bis 72 Stunden, bei einer Temperatur von 20 bis 90 °C, vorzugsweise von 30 bis 50 °C.

11. Verfahren nach einem der vorangehenden Ansprüche, wobei das hydrothermische Verfahren bei einer Temperatur von 160 °C bis 200 °C und bei einem Druck von 8 bis 15 bar durchgeführt wird.
12. Verfahren nach einem der vorangehenden Ansprüche, wobei das hydrothermische Verfahren für einen Zeitraum von 12 bis 168 Stunden, vorzugsweise von 72 bis 100 Stunden, und weiter bevorzugt nicht länger als 120 Stunden durchgeführt wird.
13. Verfahren nach einem der vorangehenden Ansprüche, wobei vor dem hydrothermischen Verfahren der asbesthaltigen Festphase Wasser oder vorzugsweise Molke zugesetzt wird.
14. Verfahren nach einem der vorangehenden Ansprüche, wobei während des hydrothermischen Verfahrens mindestens ein Chelatbildner zugesetzt wird, der beispielsweise aus Folgendem ausgewählt wird: Oxalsäure, Milchsäure, Ameisensäure oder Salze davon.

Revendications

1. Procédé pour traiter un matériau contenant de l'amiante, comprenant :

le traitement du matériau avec du petit lait de sorte à obtenir une phase liquide acide et une phase solide contenant l'amiante ;
exposer la phase solide contenant l'amiante à un procédé hydrothermal à une température comprise entre 120 °C et 250 °C et à une pression comprise entre 5 bars et 20 bars.

2. Procédé selon la revendication 1, dans lequel le petit lait est du petit lait épuisé.

3. Procédé selon l'une quelconque des revendications précédentes, dans lequel le procédé hydrothermal est réalisé à un pH compris entre 1 et 7, de préférence entre 2 à 6.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le matériau contenant l'amiante comporte de l'amiante sous forme de fibres dispersées dans une matrice fragile ou une matrice cimentaire, ou alternativement dans une matrice polymérique compacte.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le matériau contenant l'amiante comprend de l'amiante sous forme de fibres dispersées dans une matrice polymérique compacte, et dans lequel ledit matériau, avant traitement avec le petit lait, est exposé à un prétraitement thermal pour provoquer la combustion de la matrice polymérique et pour relâcher les fibres d'amiante.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le matériau contenant l'amiante est d'abord exposé à une étape de polissage.

7. Procédé selon la revendication 6, dans lequel l'étape de polissage est réalisée sur le matériau plongé dans une cuve contenant le petit lait.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel au petit lait est au moins ajouté un acide organique, en particulier de l'acide lactique ou de l'acide oxalique, de sorte à obtenir un pH compris entre 1 et 3.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le petit lait est utilisé dans une quantité comprise entre 2 et 100 fois en poids, de préférence entre 20 et 40, par rapport au poids du matériau à traiter.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel le traitement avec le petit lait est réalisé par agitation pendant une durée comprise entre 12 et 120 heures, de préférence entre 48 et 72 heures, à une température comprise entre 20 et 90 °C, de préférence entre 30 et 50 °C.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le procédé hydrothermal est réalisé à une température comprise entre 160 °C et 200 °C et à une pression comprise entre 8 et 15 bars.

12. Procédé selon l'une quelconque des revendications précédentes, dans lequel le procédé hydrothermal est réalisé

EP 2 428 254 B1

pendant une durée comprise entre 12 et 168 heures, de préférence entre 72 et 100 heures, ou mieux encore sans être supérieure à 120 heures.

5 13. Procédé selon l'une quelconque des revendications précédentes, dans lequel, avant que ne soit réalisé le procédé hydrothermal, de l'eau ou de préférence du petit lait est ajouté à la phase solide contenant l'amiante.

10 14. Procédé selon l'une quelconque des revendications précédentes, dans lequel est ajouté, lors du procédé hydrothermal, au moins un agent chélatant sélectionné par exemple à partir : d'un acide oxalique, acide lactique, acide formique, ou de leurs sels.

10

15

20

25

30

35

40

45

50

55

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Non-patent literature cited in the description

- **S.E. FAVERO-LONGO ; M. GIRLANDA ; R. HONEGGER ; B. FUBINI ; R. PIERVITTORI.** *Myco-logical Research*, 2007, vol. 111 (4), 473-481 **[0014]**
- *Fresenius Environmental Bulletin*, 2006, vol. 15 (7), 640-643 **[0015]**