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(11) **EP 1 671 682 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**21.06.2006 Bulletin 2006/25**

(51) Int Cl.:  
**A62D 3/00 (2006.01)**

(21) Application number: **04293047.9**

(22) Date of filing: **20.12.2004**

(84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR  
HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR**  
Designated Extension States:  
**AL BA HR LV MK YU**

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(54) **Asbestos degradation process with alkali metal hydroxides**

(57) The present invention relates to a process for degrading asbestos-containing materials comprising the following steps:

(a) the asbestos-containing materials and one or more solid alkali metal hydroxides are added to a

reactor; and

(b) the mixture prepared in step (a) is heated to a temperature of between about 170° C and about 580°C for at least about 10 minutes.

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**Description**

**[0001]** The present invention relates to a process for degrading asbestos-containing materials (ACMs) by mixing them with one or more alkali metal hydroxides and heating the mixture to a temperature at which it is molten in order that the alkali metal hydroxide(s) may chemically degrade the asbestos in the ACMs.

Background to the invention

**[0002]** The amount of asbestos-containing wastes is constantly increasing, since the health risks of asbestos fibres are proven and large amounts of asbestos-containing construction materials, which were widely used during the 1950s to 1970s, are being removed during the clean-up of contaminated sites. In the future even greater amounts of asbestos-containing materials (ACM) can be expected to accumulate, because legal criteria concerning asbestos abatement are being steadily tightened [Germany: TRGS 519: Technische Regel für Gefahrstoffe - Asbest ; France: Circulaire n° 96-60 of 19/07/96 ; UK: Regulation on control of pollution, 1974], rendering obligatory the disposal of existing asbestos-containing building materials.

**[0003]** Today a major part of the asbestos-containing wastes is landfilled without further treatment. This is not an optimal solution, because asbestos fibres are chemically inert and can be released, when the landfill gets damaged.

**[0004]** Destruction of asbestos minerals is intrinsically difficult due to the stability of the minerals against chemical, thermal and mechanical stress. Because of the thermal and chemical resistance of asbestos fibres most other mineral components of ACMs are decomposed faster than asbestos. Often asbestos fibres are located in a matrix of mineral building materials, so that the fibres cannot be decomposed before the matrix material is dissolved and the fibres are uncovered.

**[0005]** It is however possible to destroy asbestos-containing materials (ACM) by thermal treatment. Although at temperatures of 900°C or less, disintegration of siliceous groups into recrystallised oxide mixtures is detectable, complete disintegration of ACM is very slow, and thus a temperature above the melting temperature of asbestos (1200 - 1500°C) is normally needed to ensure degradation over a practical timescale. An example of such a process is described by DE-4418410.

**[0006]** Clearly, it would be preferable to avoid having to carry out the disintegration of ACMs at such high temperatures, given that attaining and maintaining such high temperatures requires a considerable amount of energy to be expended.

**[0007]** Amongst other problems known from prior art processes for degrading ACMs is the question of undesirable gas production. During pyrolysis of certain materials that may be combined in asbestos-containing wastes, gases such as CO<sub>2</sub> and SO<sub>2</sub> may be produced. The production of such gases, whether it be by chemical reaction within the reactor used to degrade ACMs, or as a result of the burning of fuels for heating of the reactor, complicates the management of the disintegration process. Furthermore, the gases produced within the reactor can complicate process control by foaming of the heated reaction mixture.

**[0008]** It is also desirable, given the large-scale industrial nature of ACM clean-up operations, that if any extra chemical agents are to be added to the ACMs to induce asbestos disintegration, these agents should be as inexpensive as possible. Furthermore, it is of considerable interest to be able to recycle or regenerate both the agent added to induce degradation of ACMs, and any building materials that it may be possible to recycle after degradation of the asbestos.

Summary of the invention

**[0009]** It has now surprisingly been found, and this constitutes the basis of the present invention, that asbestos-containing materials (ACMs) can be very efficiently degraded by a process which is economical in that it does not require heating to an excessively high temperature, uses relatively inexpensive materials, minimises the problematic production of exhaust gases, and has the advantage of enabling the recycling of building materials within the ACMs as well as the agent (alkali metal hydroxide(s), MOH) used to induce degradation of asbestos in the context of the present invention.

**[0010]** The process for degrading asbestos-containing materials according to the present invention comprises the following steps:

- (a) the asbestos-containing materials and one or more solid alkali metal hydroxides are added to a reactor; and
- (b) the mixture prepared in step (a) is heated to a temperature of between about 170°C and about 580°C for at least about 10 minutes.

**[0011]** In the context of the present invention, the term "mixture" is understood as meaning that the ACMs and solid alkali metal hydroxide(s) are in intimate contact, without necessarily being actually mixed.

**[0012]** It is indeed not essential that the ACMs and solid alkali metal hydroxides be (intimately) mixed in order to ensure maximum homogeneity. Indeed, in the context of asbestos decontamination, it may well be preferable to avoid physically

mixing the two materials in order to reduce the dust hazard associated with a homogenisation procedure. However, the (intimate) mixing of ACMs and solid alkali metal hydroxides naturally improves contact between the reacting materials and therefore reduces the process time, and such homogenisation may be of particular utility when carrying out ACM degradation on an industrial (tonne) scale.

#### Brief description of the Figures

##### **[0013]**

In Figure 1, a schematic diagram is provided illustrating the dissolution of asbestos-containing materials in an alkali hydroxide melt according to the process of the present invention.

In Figure 2, an alternative to the process of Figure 1 is illustrated.

Figure 3 is a scanning electron microscopy (SEM) picture showing the absence of fibres of the asbestos-containing material (ACM) sprayed asbestos coating prior to asbestos degradation treatment.

Figure 4 is a scanning electron microscopy (SEM) picture showing fibres of the asbestos-containing material (ACM) sprayed asbestos coating after asbestos degradation treatment using an alkali hydroxide melt according to the process of the present invention.

#### Detailed description of the invention

**[0014]** In the context of the present invention, any solid alkali metal hydroxide, including lithium hydroxide (LiOH), sodium hydroxide (NaOH) and potassium hydroxide (KOH) may be used, since all of these are capable of giving rise to the desired asbestos-degrading effect at appropriate temperatures.

**[0015]** However, for economic reasons, sodium hydroxide (NaOH) and potassium hydroxide (KOH) will be preferred, and sodium hydroxide (NaOH), often referred to as caustic soda, will be particularly preferred. It should also be noted that, in view of the fact that a mixture of caustic soda and potassium hydroxide shows a considerably lower melting point than either of the two hydroxides taken alone, an NaOH/KOH mixture also constitutes a preferred embodiment of the present invention, since the melting of the hydroxide is necessary in order for the asbestos degradation reaction to be efficient. A weight ratio of NaOH to KOH of about 60:40 to about 40:60 will generally be used, a weight ratio of about 50:50 being preferred, since this ratio of NaOH to KOH provides the lowest melting points (a eutectic mixture with a melting point of 170°C is obtained for 51.5% NaOH and 48.5 % KOH).

**[0016]** In the present invention, degradation of ACMs by alkali metal hydroxides is possible starting from temperatures as low as about 170° C. However, in order to achieve an optimal balance of reaction time and reaction efficiency, the preferred reaction temperature for the process of the present invention with caustic soda will lie between about 320°C and about 550°C, preferably between about 400°C and about 500°C. Concerning the duration of the ACM-degradation reaction, this duration will preferably lie between about 10 minutes and about 1 day, even more preferably between about 20 minutes and about 5 hours, and most preferably between about 30 minutes and about 60 minutes.

**[0017]** As regards the relative quantities of the reactants in the ACM-degradation reaction, the ratio of the weight of alkali metal hydroxide to the weight of asbestos-containing materials will preferably lie between about 3:1 and about 10:1, most preferably between about 3:1 and about 5:1.

**[0018]** There are no absolute minimum or maximum amounts of ACM that may be treated in the context of the process of the present invention. Small-scale (gram) or medium-scale (kilogram) treatments can be envisaged, as well as large-scale industrial treatments where tonnes of reagents are involved. In the latter case, the only limit is provided by the sizes of industrial reactors.

**[0019]** In view of the highly corrosive nature of alkali hydroxide melts, the skilled person putting into practice the process of the present invention will choose a reactor made of a material resistant to such caustic conditions. Examples of preferred reactor materials which can be used for the process of the present invention include carbon and alloyed steels, standard steel, nickel alloys, graphite and silver.

**[0020]** A preferred material for the reactor in the context of the present invention is standard steel, in the form of barrels. These have been observed by the inventors to show abrasion rates of approximately 0.5 µm per hour with caustic soda melt at 450°C. With a process time of less than 5 h and a wall thickness tolerance of 0.2 mm, the steel barrels may thus be used at least 75 times as reactor vessel for ACM dissolution in a caustic soda melt. Furthermore, at the end of their economic life-time, the used barrels can be recycled as scrap metal and replaced by new barrels. Because of the low unit costs of standard steel barrels and the low installation costs for the melt reactor, the use of standard steel barrels provides a cost effective process route for the decomposition of ACMs with caustic soda melts.

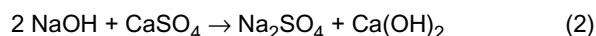
**[0021]** It is possible to use various heating means to achieve a suitable reaction temperature for the asbestos-decomposition reaction of the present invention. Classical heating means such as electroheating, induction heating, infrared heating or gas burners may thus be used.

**[0022]** In a preferred embodiment of the present invention, heating by microwaves is used for at least part of the overall heat energy introduced into the reactive mixture. Microwave heating provides the advantage of heating the reaction mixture in its heart, whereas many traditional heating processes necessarily heat the reaction mixture from the outside. The use of microwave heating also enables the problematic large-scale production of exhaust gases to be avoided, which is a disadvantage associated with gas burners, as are widely used to produce high temperatures in glass melting furnaces. Microwave sources for heating the reaction mixture in the present invention include a magnetron or klystron, and irradiation of the reaction mixture is carried out via a microwave heating hood.

**[0023]** In a particularly preferred embodiment of the present invention, a mixture of microwave and non-microwave heating methods are used to achieve and maintain a suitable reaction temperature. Any relative percentages of heat energy contributed by the microwave- with respect to the non-microwave heating source can be envisaged. However, when used in combination with steel reactor vessels, it is preferred that the relative amount of microwave energy does not exceed 50% of the total heating energy.

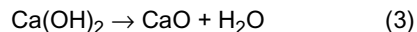
**[0024]** However, particularly if vessels (reactors) other than steel vessels (steel reactors) are used, relative amounts of microwave energy exceeding 50% of the total heating energy are possible, up to and including 100%, i.e. microwaves are used as the sole source of heat energy.

**[0025]** The major part of the ACM components in building materials is formed by lime ( $\text{CaCO}_3$ ) and gypsum ( $\text{CaSO}_4$ ). Sources of lime and gypsum-containing ACMs in buildings include asbestos cement pipes, panels and shingles, asbestos concrete parts, insulating cardboards and fibre reinforced plaster. The decomposition of these materials in alkali hydroxide melts is believed to be performed in the context of the process of the present invention by a substitution reaction of the metal ions according to the following equations (1) and (2):

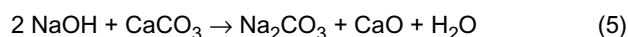
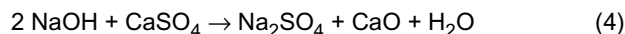


**[0026]** The sodium hydroxide is thus transformed into carbonate or sulfate whilst the lime and gypsum are transformed into calcium hydroxide.

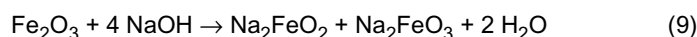
**[0027]** At temperatures above  $500^\circ\text{C}$  calcium hydroxide decomposes into calcium oxide and water according to the following equation (3):



**[0028]** Hence the total reaction is thus believed to run according to the following equations (4) and (5):



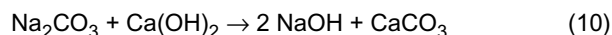
**[0029]** Silica from silicates, alumina and iron oxide are thought to be dissolved by caustic soda melts according to the following equations (6) to (9):



**[0030]** One of the advantages of the present invention is that gases that may be released during the asbestos degradation process, notably  $\text{CO}_2$  and  $\text{SO}_2$ , are trapped by the alkali metal hydroxide melt, and are therefore not released as exhaust gases. A part of these gases (notably  $\text{CO}_2$ ) may arise from organic substances in the ACM.

**[0031]** It is found that the reaction of lime and gypsum in caustic soda melts is reversible. By dissolution of the reaction product in water the path of the reaction can be reversed, lime and gypsum can be re-precipitated from the solution and caustic soda can be regained. The re-precipitation of lime and gypsum occurs in the form of fine particles

**[0032]** This reversal of the reaction can be represented schematically as follows:





**[0033]** Thus, in a preferred embodiment of the process according to the present invention, in a subsequent step (c), the used alkali metal hydroxide is recycled. This can be done by e.g. dissolution of the reaction mixture in water, separation of liquid/solid phases and recrystallisation of solid alkali metal hydroxide from aqueous solution.

**[0034]** The percentage of alkali metal hydroxide recovered, in the context of step (c) in the present invention, varies from about 60% to about 99%, most commonly between about 60% to about 90%. The exact percentage is dependent on the ratio of alkali metal hydroxide to ACM. When a high ratio of alkali metal hydroxide to ACM is used, a higher recovery rate of alkali metal hydroxide is naturally observed, because an increasing part of the alkali metal hydroxide is in chemical excess and is not consumed during the ACM degradation process.

**[0035]** It is also possible to recover lime ( $\text{CaCO}_3$ ) and gypsum ( $\text{CaSO}_4$ ) in the context of the present invention. This may be useful for "inerting" solid carbonate and sulphate residues, either for their environmentally friendly disposal, or in order to re-use them, for example as construction materials.

**[0036]** An example of a process scheme according to the present invention is provided in Figure 1.

**[0037]** In the process illustrated schematically by Figure 1, a steel barrel (1) is filled with ACM (2). This can be done at the ACM removal site or at the ACM treatment plant. If the barrel is filled at the ACM removal site the steel barrel can be sealed to ensure safe transport.

**[0038]** In a filling station (3), solid alkali hydroxide (4) is added to the barrel containing ACM. Then, the filled barrel is moved to the heating station (5) where it is heated to form a melt (6).

**[0039]** When the alkali hydroxide is molten it infiltrates and decomposes the asbestos containing material and the asbestos fibres are destroyed. The resulting molten solution is then dissolved in water in a dissolution reactor (9). The product of the dissolution reactor is conducted into a solid/liquid separator (10), e.g. a filter or a centrifuge. The solid product of the separation process (11) consists mainly of lime, gypsum and silica and can be recycled e.g. in the cement industry. The liquid product of the separation process is transferred into an evaporator (12), where it is concentrated. Then, the alkali hydroxide is recovered in a crystallizer (13). The recycled alkali hydroxide (4) can be reused in the filling station (3).

**[0040]** Another embodiment of the process according to the invention is provided in Figure 2. The process illustrated in Figure 2 is identical to the one illustrated in Figure 1, except that in addition to conventional heating of the barrel surface, microwave heating is used to accelerate and homogenize the heating process. The microwave radiation is produced in a microwave source (7), e.g. a magnetron or klystron, and irradiated into the steel barrel by a microwave heating hood (8).

## Examples

### Example 1

**[0041]** This example demonstrates the dissolution of different building materials (lime bricks, clinker, gypsum, clay, mortar, marble, cement, concrete, glass, quartz) in a caustic soda melt.

**[0042]** 50g of mixed building materials and 200g NaOH were heated in an electro furnace to 400°C for 15 hours in a steel vessel (steel reactor). In this example, a conventional source of heat was used.

**[0043]** At the end of this period, it was observed that all the mixed mineral building materials (lime bricks, clinker, gypsum, clay, mortar, marble, cement, concrete, glass, quartz) were completely dissolved. (The plastic and wood present produced some charcoal.)

### Examples 2-5

**[0044]** Examples 2-5 demonstrate the ability of alkali hydroxide melts to dissolve asbestos in ACMs.

**[0045]** Table 1 demonstrates the ACMs used, the amounts of ACM and alkali metal hydroxide, the temperature and reaction time, as well as the results observed for a number of representative examples of the dissolution of asbestos in melts according to the present invention. In each of the reactions illustrated in Examples 2-5, only microwave heating was used.

**[0046]** Here, the techniques of X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX), were used to analyse the effective degradation of asbestos-containing materials in alkali metal hydroxide melts.

**[0047]** The application of X-ray diffraction (XRD) allows a quantitative determination of crystalline phases like asbestos minerals to less than one weight percent.

**[0048]** Manual scanning electron microscopy methods (SEM) are commonly used to detect asbestos fibres. This

method is used for detecting inorganic fibres with geometric diameters down to 0.2  $\mu\text{m}$  and lengths down to 2.5  $\mu\text{m}$ .

**[0049]** With the help of energy dispersive X-ray analysis (EDX), it is possible to distinguish between asbestos and other inorganic fibres, so that just asbestos fibres are counted.

**Table 1: Experiments demonstrating the ability of alkali hydroxide melts to dissolve asbestos in ACMs**

| Ex | ACM             | Mass of ACM / g | Alkali metal hydroxide MOH | Mass of MOH / g | Reaction temp. / °C | Reaction time / min | Results  |
|----|-----------------|-----------------|----------------------------|-----------------|---------------------|---------------------|--|
| 2  | Sprayed coating | 3.0             | NaOH                       | 13.7            | 450                 | 30                  | No fibres visible, no fibres detectable with EDX-, SEM- and XRD-analysis |
| 3  | Gypsum          | 9.0             | NaOH                       | 36              | 400                 | 45                  | No fibres visible, no fibres detectable with EDX-, SEM- and XRD-analysis |
| 4  | Eternit®        | 6.0             | NaOH                       | 24              | 400                 | 45                  | No fibres visible, no fibres detectable with EDX-, SEM- and XRD-analysis |
| 5  | Gypsum          | 6.0             | NaOH                       | 25              | 400                 | 45                  | No fibres visible, no fibres detectable with EDX-, SEM- and XRD-analysis |

#### Example 6

**[0050]** This example demonstrates the decontamination of ACM with combined microwave and infra-red heating in a steel drum. 6 kg of sprayed asbestos coating are mixed with 25 kg of caustic soda and treated at 400 °C for 90 minutes.

**[0051]** Figures 3 and 4 show a comparison between sprayed asbestos coating before and after treatment by NaOH melt. In the SEM pictures, the destruction of the asbestos fibres is evident.

#### Example 7

**[0052]** This example relates to the determination of degradation rates for steel and lime in a caustic soda melt.

**[0053]** A piece of marble (a massive form of lime) and two steel plates were combined with a large excess of NaOH (sufficient to encase all parts if molten). The mixture was heated to 450°C for 15 hours in a steel vessel as the reactor.

**[0054]** In this experiment, the following degradation rates were observed:

- marble: 5mm degradation in 15 hours = 330  $\mu\text{m/h}$
- steel: 10  $\mu\text{m}$  degradation in 15 hours = 0.67  $\mu\text{m/h}$

**[0055]** In conclusion, it is seen that:

1. Lime particles with a diameter of 4 mm could be dissolved in a caustic soda melt within 6 hours.
2. Steel barrels with a wall thickness tolerance of 0.2 mm could be used at least 20 times at 15 hours treatment time (or 75 times at 4 hours treatment time).

#### Example 8

**[0056]** In this example, the possibility of recovering  $\text{CaCO}_3$  and sodium hydroxide after a process according to the present invention was studied.

**[0057]** In particular, lime was dissolved in caustic soda melt and then re-precipitation was carried out in aqueous solution. In the heating step, 10 g of  $\text{CaCO}_3$  and 40 g of NaOH were mixed and heated to 400°C for 15 hours in a steel vessel. Then, the cold melt was dissolved in water. Subsequently, after sedimentation of the re-precipitated lime and decantation of the clear solution, the product was dried at 300°C

**[0058]** Here, it was observed that 8.8 g of the  $\text{CaCO}_3$  was re-precipitated product, i.e. 88% of the lime dissolved in the caustic soda melt was recycled. Since each mol of  $\text{CaCO}_3$  recovered means two mol of NaOH recovered according to the equation  $(\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightarrow 2 \text{NaOH} + \text{CaCO}_3)$ , this means that it is expected that 88% of the NaOH initially consumed may also be recovered.

#### **Claims**

1. Process for degrading asbestos-containing materials comprising the following steps:

- (a) the asbestos-containing materials and one or more solid alkali metal hydroxides are added to a reactor; and
- (b) the mixture prepared in step (a) is heated to a temperature of between about 170° C and about 580°C for at least about 10 minutes.

2. Process according to claim 1, wherein the solid alkali metal hydroxide is sodium hydroxide (NaOH).

3. Process according to claim 1, wherein the solid alkali metal hydroxide is potassium hydroxide (KOH).

4. Process according to claim 1, wherein a mixture of solid sodium hydroxide (NaOH) and potassium hydroxide (KOH) is used.

5. Process according to any of claims 1 to 4, wherein the reaction temperature lies between about 320°C and about 550°C, preferably between about 400°C and about 500°C.

6. Process according to any of claims 1 to 5, wherein the duration of the reaction in step (b) lies between about 10 minutes and about 1 day, more preferably between about 20 minutes and about 5 hours, and most preferably between about 30 minutes and about 60 minutes.

7. Process according to any of claims 1 to 6, wherein the ratio of the weight of solid alkali metal hydroxide to the weight of asbestos-containing materials lies between about 3:1 and about 10:1, preferably between about 3:1 and about 5:1.

8. Process according to any of claims 1 to 7, wherein the reaction mixture in step (b) is heated by electroheating, induction heating, infrared heating or gas burners.

9. Process according to any of claims 1 to 7, wherein the reaction mixture in step (b) is heated by a combination of both microwave irradiation and one or more of electroheating, induction heating, infrared heating and gas burners.

10. Process according to any of claims 1 to 9, wherein in a subsequent step (c), the used alkali metal hydroxide is recycled.

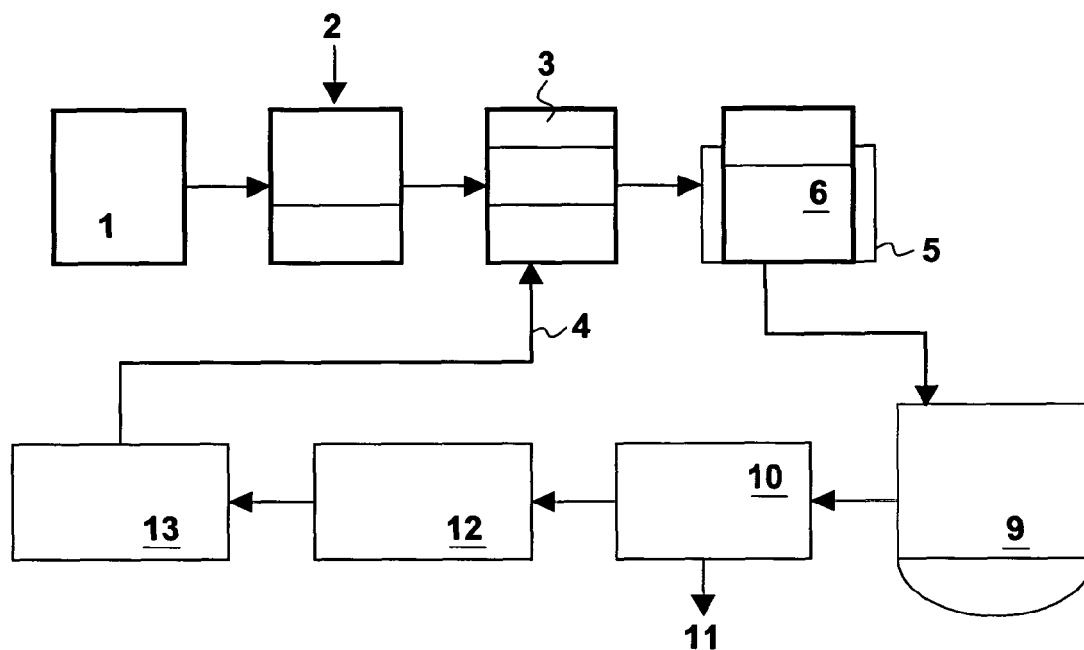


FIG.1

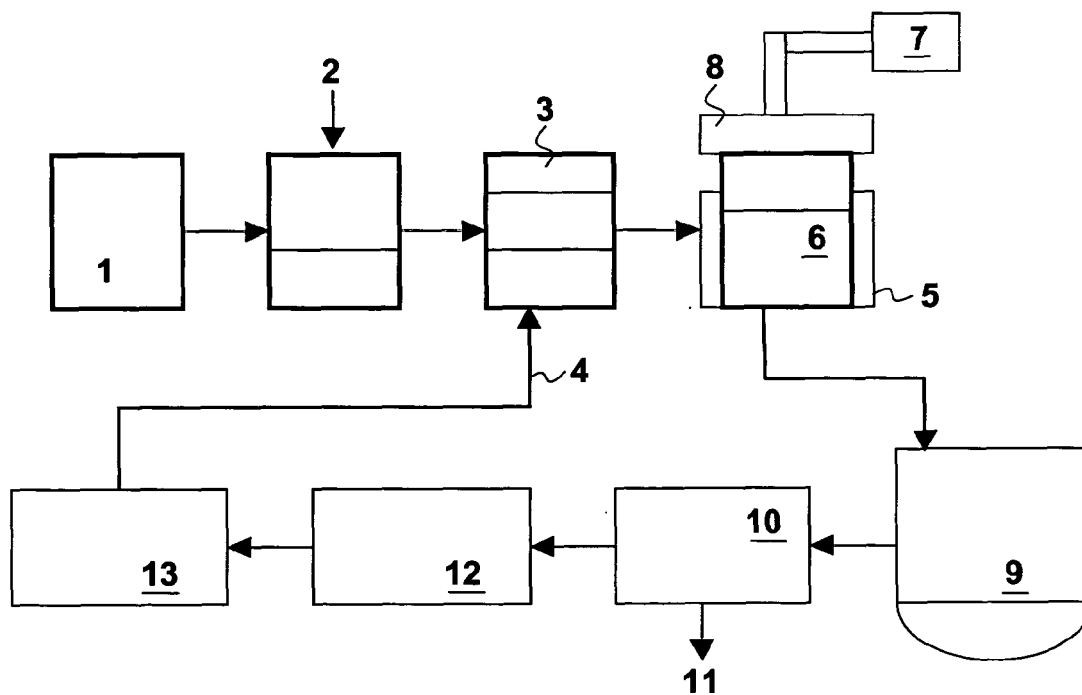


FIG.2



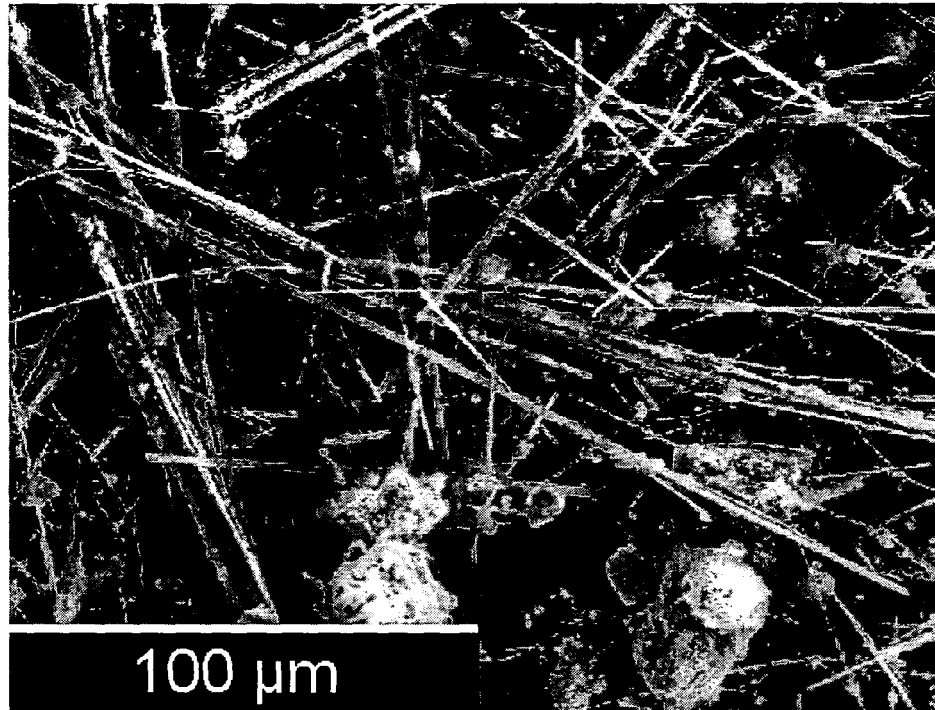


Figure 3. Sprayed asbestos coating before treatment

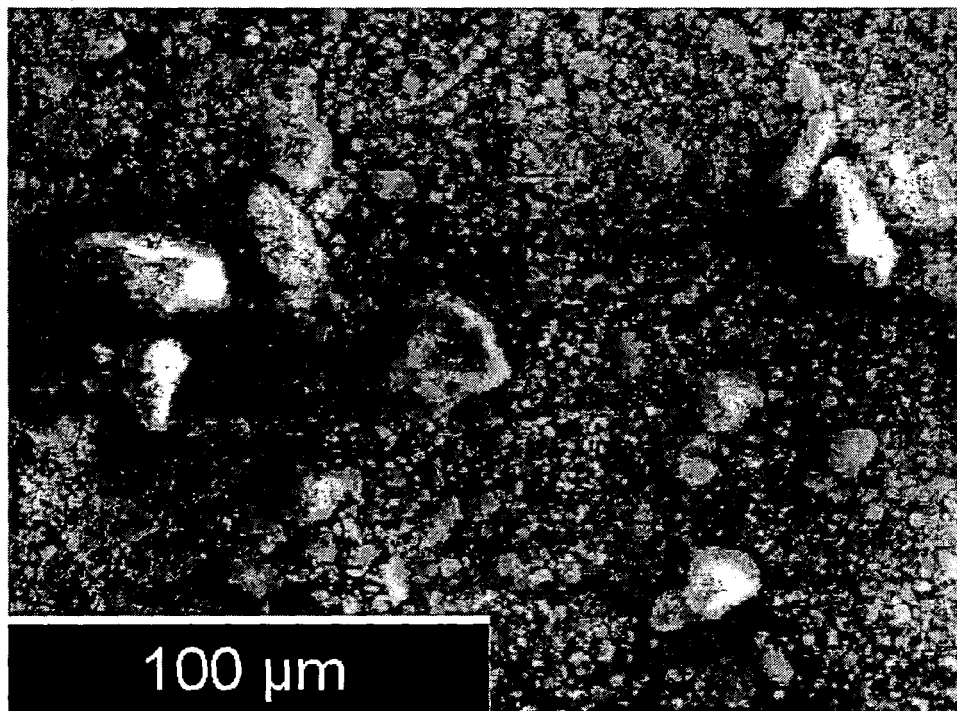


Figure 4. Sprayed asbestos coating after treatment with NaOH



European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 04 29 3047

| DOCUMENTS CONSIDERED TO BE RELEVANT   |   |  |  |
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|   |   |  | TECHNICAL FIELDS SEARCHED (Int.Cl.7)         |
|   |   |  | A62D   |
| The present search report has been drawn up for all claims  |   |  |  |
| Place of search<br><b>The Hague</b>   |   | Date of completion of the search<br><b>24 June 2005</b>  | Examiner<br><b>Dalkafouki, A</b>             |
| <b>CATEGORY OF CITED DOCUMENTS</b><br>X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |   | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>& : member of the same patent family, corresponding document |  |

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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24-06-2005

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