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(54) **Noxious component removal process and system**

Verfahren und System zur Entfernung von Schadstoffen

Procédé et système d'élimination des composés nocifs

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(56) References cited:
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US-A- 4 938 936

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Description**BACKGROUND OF THE INVENTION****1. Field of the Invention**

[0001] This invention relates to improvements in a process for removing a noxious component (such as chlorine and/or sulfur) from a material (referred to as "treatable material") containing chlorine and or sulfur, such as urban waste or trash and industrial waste, and to improvements in a noxious component removal agent to be used in the process, and more particularly to a technique in which the noxious component removal agent is reacted with noxious component-containing gas (hydrogen chloride, chlorine gas and/or sulfur oxide gas) generated upon thermal treatment of the trash and waste to form harmless gas and compounds.

2. Description of the Prior Art

[0002] Recently waste such as urban waste or trash are increasing in its amount year by year so that its treatment is becoming problematic. Such urban waste includes waste or trash from general homes and offices and therefore is mainly constituted of combustible waste. This combustible waste includes a variety of chemical substances (for example, plastic) containing a large amount of polyvinyl chloride, and a variety of materials (for example, paper used in offices) containing a large amount of chlorine components such as chlorine-containing bleaching agent.

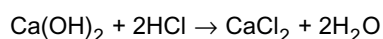
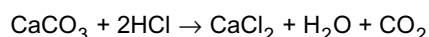
[0003] In general, incineration has been usually employed for treating such waste. However, when the waste or treatable material containing chlorine components is incinerated, chlorine-containing gas such as hydrogen chloride gas and chlorine gas is generated thereby raising problems of environmental pollution and deterioration of incinerating facility under the action of the chlorine-containing gas. For the purpose of suppressing generation of such chlorine-containing gas, it has been carried out to incinerate the waste or treatable material upon adding thereto a chlorine removal agent such as slaked lime, calcium carbonate or the like as disclosed, for example, in Japanese Patent Publication No. 2-10341. Additionally, it has been also known that after the treatable material cast in an incinerator is subjected to an incineration treatment, emitted gas undergoes a variety of purification treatments as occasion demands, for example, is introduced into a bag filter so as to be reacted with slaked lime thus preventing noxious chlorine-containing gas from being emitted to the atmospheric air.

[0004] As discussed above, in case of incineration of the waste or treatable material, the chlorine-containing substances such as chloride and other chlorine compounds are problematic, in which chlorine-containing gas generated in the course of incineration damages the incinerator itself and corrodes steam pipes and further leads to problems of producing dioxin which is virulently poisonous. Accordingly, chlorine-containing gas has been usually reacted with slaked lime or the like in the bag filter thereby being prevented from being emitted to the atmospheric air. Such measures can be expected to obtain a certain effect under treatment of burnt gas so that chlorine-containing gas can be prevented from being dispersed to the atmospheric air. However, it is difficult to completely remove chlorine-containing substances by such measures because chlorine-containing substances remain in a residue formed after incineration of the treatable material. This forms part of cause of generating dioxin. Even by the measure of adding slaked lime or calcium carbonate during the incineration, chlorine-containing gas has not been able to be sufficiently prevented from its generation.

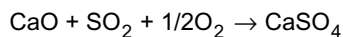
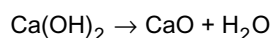
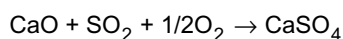
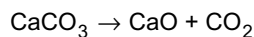
[0005] Further, it has been proposed that alkali material is sprayed into the incinerator in which the treatable material is incinerated as disclosed, for example, in Japanese Patent Provisional Publication No. 54-93864. In this proposition, however, chlorine-containing gas which has been once generated and filled in the incinerator is treated, which is similar to the above measure and therefore renders it impossible to completely remove chlorine-containing gas.

[0006] Furthermore, it has been also proposed that incineration of the treatable material is accomplished upon adding thereto alkali material containing calcium such as lime (CaCO_3), slaked lime (Ca(OH)_2) or the like, or that SO_x is passed through a filter filled with the alkali material to remove SO_x as disclosed, for example, in Japanese Patent Publication No. 2-10341, Japanese Patent Provisional Publication No. 1-296007, and Japanese Patent Provisional Publication No. 59-12733. Reactions made in these propositions are as follows:

[0007] In case of treatment of chlorine-containing gas (HCl):



[0008] In case of treatment of sulfur oxide containing gas (SO_2):



[0009] Besides, it has also been proposed to cause the treatable material to be subjected to thermal decomposition or dry distillation in place of incineration, thereby reducing the volume of the treatable material and carbonizing the treatable material, as disclosed in Japanese Patent Provisional Publication No. 5-33916, Japanese Patent (Kohyo) Publication No. 8-510789, and Japanese Patent Provisional Publication No. 9-155326. Additionally, the Japanese Patent Provisional Publication No. 5-33916 discloses spraying alkali material such as slaked lime into a furnace; however, no sufficient effect of removing chlorine-containing gas can be expected because the alkali material is brought into contact with chlorine-containing gas which has been once generated and filled in the furnace.

[0010] EP-A-0 372 276 discloses a process for the recovery of clean hydrocarbon stock from hydrocarbon oil contaminated among others with chlorinated compounds. The contaminated oil is subjected to a thermal or catalytic cracking treatment followed by a separation of the distillate containing chlorine compounds and a hydrogenating refining step of the chlorine compounds-containing distillate. During the thermal or catalytic treatment sodium hydroxide may be added.

[0011] WO 96/29118 A discloses a method for treating halogen-containing waste material with an alkali or alkaline earth compound. The material and the compound can be mixed and then the mixture is heated in a reaction zone in a substantially closed system, so as to establish a controllable autogenous pressure.

[0012] In view of the above, it has been eagerly desired to hasten establishment of techniques for sufficiently removing chlorine-containing gas or sufficiently preventing chlorine-containing gas from generation even upon thermal treatment of the treatable material, which chlorine-containing gas forms part of cause of production of dioxin which is known as being virulently poisonous for human body.

BRIEF SUMMARY OF THE INVENTION

[0013] As a result of a variety of experiments and investigations for removing noxious chlorine-containing substances or gases (such as hydrogen chloride gas and chlorine gas) in emitted gas generated upon thermal treatment of a waste or treatable material containing a large amount of chlorine components or compounds, the inventors of the present invention have found that the noxious chlorine-containing substances or gases can be effectively reacted with a sodium or potassium compound (particularly sodium and potassium carbonate, hydrogen carbonate and hydroxide) so that the noxious chlorine-containing gases are effectively converted into harmless chlorides. Additionally, it has been confirmed that the sodium or potassium compound is also effective for converting noxious sulfur-containing gases into harmless sulfite.

[0014] The present invention has been envisaged depending upon the above knowledge and to provide an improved noxious component removal process using a particular noxious component removal agent containing a sodium or potassium compound, in which noxious component-containing gases generated upon heating the treatable material are immediately reacted with the noxious removal agent thereby to form harmless compound, preventing emission of noxious component-containing gas into the atmospheric air.

[0015] It is an object of the present invention to provide an improved noxious component removal process which can overcome drawbacks encountered in conventional similar noxious component removal processes.

[0016] Another object of the present invention is to provide an improved noxious component removal process to be applied in a thermal treatment process for a waste or treatable material, by which generally no noxious component-containing gas is contained in emitted gas and also in a residue formed upon the thermal treatment of the treatable material, thereby generally completely preventing noxious substances (including dioxin) from being generated in the thermal treatment process.

[0017] Another object of the present invention is to provide an improved noxious component removal process in which noxious component-containing gas generated upon thermal treatment of a waste or treatable material can be generally completely removed during the thermal treatment thereby omitting the possibility of generating noxious substances (including dioxin), while a residue contains only harmless compound without containing noxious component-containing substances.

[0018] A first aspect of the present invention resides in a process for removing at least one of chlorine and sulfur

from a treatable material containing at least one of chlorine and sulfur, comprising the following steps in the sequence set forth:

5 mixing the treatable material and a chlorine and sulfur removal agent to form a mixture, the chlorine and sulfur removal agent containing at least one compound selected from the group consisting of a sodium compound and a potassium compound;
 supplying the mixture into a furnace;
 stirring the mixture in the furnace; and
 10 heating the mixture in a low oxygen concentration atmosphere in the furnace to thermally decompose the treatable material to generate at least one of a chlorine-containing substance and a sulfur-containing substance and cause at least one of the chlorine-containing substance and the sulfur-containing substance to contact and react with said chlorine and sulfur removal agent to form at least one of harmless chloride and sulfite.

15 **[0019]** The present invention resides especially in a process wherein chlorine is removed from a treatable material containing chlorine.

[0020] A second aspect of the present invention resides in a system for removing at least one of chlorine and sulfur from a treatable material containing at least one of chlorine and sulfur, comprising:

20 a device for mixing the treatable material and a chlorine and sulfur removal agent to form a mixture, the chlorine and sulfur removal agent containing at least one compound selected from the group consisting of a sodium compound and a potassium compound;
 a furnace into which said mixture of the treatable material and said chlorine and sulfur removal agent is supplied, said furnace being adapted to form therein a low oxygen concentration atmosphere and being provided with a rotating transferring means; and
 25 a heating device for heating said mixture in the low oxygen concentration atmosphere in said furnace to thermally decompose the treatable material so as to accomplish dry distillation of said treatable material, in which said mixture generates at least one of a chlorine-containing substance and a sulfur-containing substance and cause at least one of the chlorine-containing substance and the sulfur-containing substance to contact and react with the chlorine and sulfur removal agent to form at least one of harmless chloride and sulfite.

30 **[0021]** According to the noxious chlorine and/or sulfur component removal process of the present invention, no generation of noxious component-containing gas is made throughout whole steps in a thermal treatment process of the treatable material and throughout whole temperature ranges in the thermal treatment process, which has not been achieved by conventional noxious component removal processes which use slaked lime or calcium carbonate as the chlorine removal agent. Additionally, the residue formed upon thermal treatment of the treatable material contains no noxious component-containing substances, containing harmless compound (such as chloride and/or sulfite). Thus, the noxious component removal process of the present invention exhibits a high noxious component removal effect particularly for the treatable material containing a large amount of noxious component-containing substances or compounds of the noxious component, such as urban waste or trash.

35 **[0022]** In the noxious component removal process of the present invention, the noxious component removal agent of the present invention is mixed with the treatable material so as to immediately react with noxious component-containing gas generated upon heating the treatable material, thereby to form harmless gas and compound of the noxious component.

40 **[0023]** By virtue of the fact that noxious component-containing gas can be generally completely removed in the furnace for thermal treatment of the treatable material, a thermal treatment furnace (including an incinerator) itself, steam pipes and the like can be effectively prevented from being corroded, thereby prolonging life of the furnaces and the facilities. Additionally, it is to be noted that the residue formed upon heating the treatable material do not contain dioxin which is virulently poisonous for human body, thus largely improving safety from the circumferential and treatment-operational viewpoints.

45 **[0024]** Furthermore, according to the noxious component removal process of the present invention, emitted gas from the furnace is harmless and combustible, and therefore the emitted gas may be reusable as fuel for a gas engine, a turbine, a boiler, a heat source of a water heating device, and fuel for a heater. Additionally, massed carbon components in the residue may be used as fuel, and inorganic materials in the residue may be reusable as the material of glass or cement. It will be appreciated that the noxious component removal process of the present invention cannot be affected even if the waste or treatable material contains water. No noxious chlorine-containing gas exists in emitted gas from the furnace, and therefore the emitted gas may be further heated to make a secondary combustion as a post-treatment for the emitted gas, as occasion demands.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] Fig. 1 is a block diagram of a chlorine and sulfur removal system for carrying out the fifth embodiment of the noxious component removal process according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0026] According to the present invention, a process for removing at least one of chlorine and sulfur from a treatable material (such as urban waste or trash, or industrial waste) containing at least one of chlorine and sulfur, comprises the following steps in the sequence set forth: mixing the treatable material and a chlorine and sulfur removal agent to form a mixture, said chlorine and sulfur removal agent containing at least one compound selected from the group consisting of a sodium compound and a potassium compound and supplying the mixture into a furnace, stirring the mixture in the furnace, and heating said mixture in a low oxygen concentration atmosphere in the furnace to thermally decompose the treatable material to generate at least one of a chlorine-containing substance and a sulfur-containing substance and cause at least one of the chlorine-containing substance and the sulfur-containing substance to contact and react with said chlorine and sulfur removal agent to form at least one of harmless chloride and sulfite.

[0027] Examples of the chlorine and sulfur removal agent (in the following designated as noxious component removal agent) to be used in the above process are:

- (1) sodium hydrogen carbonate and sodium carbonate, such as sodium hydrogen carbonate (NaHCO_3), sodium carbonate (Na_2CO_3), sodium sesqui carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), and natural soda (containing $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$);
- (2) sodium hydroxide (NaOH) and potassium hydroxide (KOH); and
- (3) potassium carbonate and potassium hydrogen carbonate such as potassium carbonate (K_2CO_3), potassium hydrogen carbonate (KHCO_3), and potassium sodium carbonate ($\text{KNaCO}_3 \cdot 6\text{H}_2\text{O}$).

[0028] It will be understood that the above-listed compounds are used singly or in combination as the noxious component removal agent. In other words, the noxious component removal agent contains at least one of sodium hydrogen carbonate, sodium carbonate, sodium sesqui carbonate, natural soda, sodium hydroxide, potassium hydroxide, potassium carbonate, potassium hydrogen carbonate, and potassium sodium carbonate, and the like.

[0029] The noxious component removal agent to be used in the form of mass, plate, porous body, particle (including power, granule, or mixture of powder and granule), solution (aqueous solution, or other solutions), or suspension. These forms are used singly or in combination.

[0030] The amount of the noxious component removal agent to be used is usually within a range of from 0.05 to 10 % by weight relative to the treatable material at a starting time which is before a time at which the treatable material is mixed with the noxious component removal agent. However, in case the treatable material including substances or compounds containing a large amount of chlorine component, such as polyvinyl chloride, polyvinylidene chloride, other chlorine-containing synthetic resins and/or chlorine-containing rubbers, the amount of the noxious component removal agent to be used is within a range of from 10 to 17 % weight relative to the treatable material at the starting time. The amount of the noxious component removal agent may be selected to be larger than the chemical equivalent of chlorine-containing substance or gas (a substance or gas containing chlorine) generated from the treatable material upon heating, regardless of the weight of the treatable material. Otherwise, the amount of the noxious component removal agent may be selected to suppress the emission levels of chlorine-containing gases below permissible emission standards. Also in case the treatable material includes substances or compounds containing a large amount of sulfur component, the amount of the noxious component is selected similarly to the above.

[0031] The noxious component removal agent is mixed with the treatable material and heated at a thermal decomposition temperature ranging from 200 to 1000 °C in a low oxygen concentration atmosphere. In other words, mixing of the noxious component removal agent and the treatable material is made before heating for thermally decomposing the treatable material, i.e., before the temperature of the treatable material rises to a level at which the thermal decomposition of the treatable material occurs. At the decomposition temperature, chlorine compounds, sulfur compounds and substances containing chlorine and/or sulfur are thermally decomposed. The low oxygen concentration atmosphere means an atmosphere in which the concentration of oxygen is low, which can be accomplished by closing the inlet and outlet of a thermal treatment furnace or tank such as a heating furnace, upon casting the mixture of the treatable material and the noxious component removal agent into the furnace. It will be understood that the low oxygen concentration atmosphere corresponds to a condition in which atmospheric air remains within the furnace whose inlet and outlet have been closed. In other words, the low oxygen concentration atmosphere corresponds to a condition in which the mixture is put in the furnace which is substantially sealed so as to prevent fresh air from being supplied into the furnace, in which a pressure in the furnace leaks out of the furnace. Accordingly, the low oxygen concentration

atmosphere does not require a complete closing or sealing state of the furnace and includes also a condition in which the side of the inlet of the furnace is closed with the treatable material itself, in which a gas pressure within the furnace is raised under heating so that supply of air from the outside of the furnace is hardly made. The low oxygen concentration atmosphere may be a thermal decomposition atmosphere in which the treatable material thermally decomposes to generate so-called thermal decomposition gas of the treatable material. Thus, the low oxygen concentration atmosphere accomplishes dry distillation of the treatable material.

[0032] It will be understood that the noxious component removal agent is basically mixed with the treatable material upon being cast or sprayed onto the treatable material in the furnace. The noxious component removal agent may be additionally cast or sprayed onto the mixture of the treatable material and the noxious component removal agent in the furnace.

[0033] As a result of the above heating in the low oxygen concentration atmosphere, substantially no gas component of chlorine-containing compounds (compounds containing chlorine) and/or sulfur-containing compounds (compounds containing sulfur) remain in emitted gas from the furnace, and therefore a post-treatment (such as a heating treatment or secondary burning) for the emitted gas can be made as occasion demands. It is a matter of course that the emitted gas may be discharged to the atmospheric air as it is.

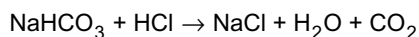
[0034] While the noxious component removal agent has been described as being mixed with the treatable material before heating or thermal decomposition of the treatable material, it will be understood that noxious component removal agent may be also effective for removing chlorine even upon contacting with dry distillation gas or emitted gas (gas generated under dry distillation of the treatable material) discharged from the furnace after heating or thermal decomposition of the treatable material.

[0035] Here, a first embodiment of the noxious component or chlorine removal process according to the present invention will be discussed. In this embodiment, the noxious component or chlorine removal agent contains alkali metal hydrogen carbonate and/or alkali metal carbonate, i.e., at least one of sodium hydrogen carbonate (NaHCO_3), sodium carbonate (Na_2CO_3), sodium sesqui carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), natural soda (containing $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$).

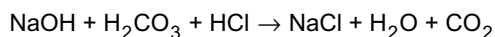
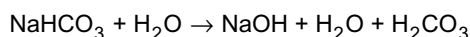
[0036] Next, discussion will be made on mechanisms of reaction between hydrogen carbonate or carbonate containing alkali metal (sodium) and chlorine-containing gas, realizing unexpected results in which both emitted gas and residue are made harmless.

(1) In case of using sodium hydrogen carbonate as the chlorine removal agent:

When sodium hydrogen carbonate (NaHCO_3) is added to the treatable material which is to generate hydrogen chloride (HCl), sodium hydrogen carbonate and hydrogen chloride react as follows:

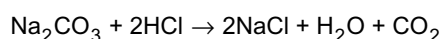


In the presence of water in reaction between sodium hydrogen carbonate and the treatable material which is to generate hydrogen chloride, reaction is made according to the following chemical equations:



(2) In case of using sodium carbonate as the chlorine removal agent:

When sodium carbonate (Na_2CO_3) is added to the treatable material which is to generate hydrogen chloride (HCl), sodium carbonate and hydrogen chloride react as follows:



(3) In case of using sodium sesqui carbonate as the chlorine removal agent:

Sodium sesqui carbonate is represented by a chemical formula, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ and can react with hydrogen chloride similarly to the cases of (1) and (2) thereby converting noxious hydrogen chloride into harmless chloride (NaCl). Sodium sesqui carbonate naturally exists as and called "trona".

[0037] Accordingly, chlorine-containing compound and chlorine component in the treatable material can be converted

into sodium chloride (NaCl), water (H₂O) and carbon dioxide gas (CO₂), and therefore hydrogen chloride forming part of a source of dioxin cannot be formed thereby realizing the unexpected result of making both emitted gas and residue harmless.

[0038] It will be appreciated that, in this embodiment, the substance containing carbonate containing an alkali metal, such as sodium carbonate, sodium hydrogen carbonate, sodium sesqui carbonate, natural soda (Na₂CO₃ • NaHCO₃ • 2H₂O) is used as the chlorine removal agent. Sodium carbonate can form monohydrate compound and decahydrate compound and is known as soda. Sodium sesqui carbonate naturally exists as trona.

[0039] As will be understood, in the heating process in which the reactions according to the above chemical reactions are made, NaCl is formed. NaCl is a harmless chloride and can be effectively removed under a rinsing or dissolving treatment with water or the like. After the rinsing treatment, solid residual materials or carbonized materials remain in the tank and reusable. Accordingly, the residual materials can be separated into respective materials which are different in characteristics by any separating means. The separated respective materials are dried and massed to be usable as fuel or the like. Additionally, liquid (such as water) used for the above rinsing treatment hardly contains noxious substances and therefore can be discharged as it is to a river and the sea.

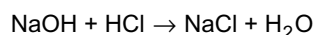
[0040] More specifically, the residue taken out from the tank contains harmless chloride or sodium chloride (NaCl). In order to extract the carbonized materials, the residue is put into a water tank containing water, and stirred for a predetermined time thereby dissolving sodium chloride. Subsequently, solid materials in the water tank are taken out from the water tank and then are subjected to a centrifugal dehydration to separate water content from the solid materials. The thus dehydrated solid materials are dried and hardened into a mass. Water remaining in the water tank and the separated water content are drained through a separate draining and treatment means. It will be appreciated that carbon contents in the hardened mass can be used as fuel while inorganic contents in the hardened mass can be used as materials for glass and cement. Further, as discussed above, the residue can be separated into respective materials which are different in characteristics by any separating means, upon which the separated respective materials are dried and massed to be effectively used as fuel or the like.

[0041] Next, a second embodiment of the noxious component or chlorine removal process according to the present invention will be discussed. In this embodiment, the noxious component or chlorine removal agent contains at least one alkali metal hydroxide, i.e., at least one of sodium hydroxide (NaOH) and potassium hydroxide (KOH).

[0042] Discussion will be made on mechanisms of reaction between alkali metal hydroxide and chlorine-containing gas, realizing unexpected results in which both emitted gas and residue are made harmless.

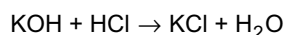
(1) In case of using sodium hydroxide (NaOH) as the chlorine removal agent:

When sodium hydroxide is added to the treatable material which is to generate hydrogen chloride (HCl), sodium hydroxide reacts with hydrogen chloride to form harmless sodium chloride and water as follows:



(2) In case of using potassium hydroxide (KOH) as the chlorine removal agent:

When potassium hydroxide is added to the treatable material which is to generate hydrogen chloride (HCl), potassium hydroxide reacts with hydrogen chloride to form potassium chloride and water, as follows:



[0043] Accordingly, chlorine-containing compound and chlorine component in the treatable material can be converted into sodium or potassium chloride and water, and therefore hydrogen chloride forming part of a source of dioxin cannot be formed thereby realizing the unexpected results of making both emitted gas and residue harmless.

[0044] As will be understood, in the heating process in which the reactions according to the above chemical reactions are made, NaCl and KCl are formed. NaCl and KCl are harmless chlorides and can be effectively removed under a rinsing or dissolving treatment with water or the like. After the rinsing treatment, solid residual materials or carbonized materials remain in the tank and reusable. Accordingly, the residual materials can be separated into respective materials which are different in characteristics by any separating means. The separated respective materials are dried and massed to be usable as fuel or the like. Additionally, liquid (such as water) used for the above rinsing treatment hardly contains noxious substances and therefore can be discharged as it is to a river and the sea.

[0045] More specifically, the residue taken out from the tank contains harmless sodium chloride (NaCl) and potassium chloride (KCl). In order to extract the carbonized materials, the residue is put into a water tank containing water, and stirred for a predetermined time thereby dissolving sodium and potassium chlorides. Subsequently, solid materials in the water tank are taken out from the water tank and then are subjected to a centrifugal dehydration to separate water

content from the solid materials. The thus dehydrated solid materials are dried and massed. Water remaining in the water tank and the separated water content are drained through a separate draining and treatment means. It will be appreciated that carbon contents in the massed solid materials can be used as fuel while inorganic contents in the massed solid materials can be used as materials for glass and cement. Further, as discussed above, the residue can be separated into respective materials which are different in characteristics by any separating means, upon which the separated respective materials are dried and massed to be effectively used as fuel or the like.

[0046] Next, a third embodiment of the noxious component or chlorine removal process according to the present invention will be discussed. This embodiment is particularly applicable to the chlorine removal process for polyvinyl chloride, polyvinylidene chloride, a synthetic resin containing chlorine, a rubber containing chlorine and/or the like. In this embodiment, the noxious component chlorine removal agent contains alkali metal hydrogen carbonate and/or alkali metal carbonate, i.e., at least one of sodium hydrogen carbonate, sodium carbonate, sodium sesqui carbonate, and natural soda. Additionally, polyvinyl chloride and polyvinylidene chloride are used as the treatable material in this embodiment.

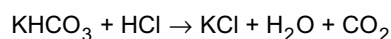
[0047] As an instance, sodium hydrogen carbonate (NaHCO_3) is used as the chlorine removal agent, in which the sodium hydrogen carbonate is mixed with the treatable material and heated thereby bringing about the following reaction with hydrogen chloride (HCl) which is a major chlorine-containing compound contained in gases generated from the treatable material upon heating: $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$. According to this reaction, if Na and CO components exist in the reaction system, chlorine reacts with Na to form NaCl which is a part of a residue formed upon heating the treatable material, and additionally water (H_2O) and gas (CO_2) are formed. As a result, no chlorine-containing gas is generated and emitted from the furnace, realizing that the emitted gas and the residue are rendered harmless. It will be understood that chlorine-containing compound or gas is a source for producing dioxin which is virulently poisonous.

[0048] According to this embodiment, when the heating treatment is applied to the treatable material containing chlorine-containing substance which will generate chlorine-containing gas upon heating, alkali metal carbonate and/or alkali metal hydrogen carbonate are added to and mixed with the treatable material as the chlorine removal agent thereby form the mixture. By heating this mixture in the low oxygen concentration atmosphere, the chlorine-containing substance is thermally decomposed at a predetermined temperature thereby generating harmful chlorine-containing gas. This chlorine-containing gas immediately reacts with the chlorine removal agent thus to form harmless chloride.

[0049] As will be understood, in the heating process in which the reactions according to the above chemical reactions are made, NaCl is formed. NaCl is a harmless chloride and can be effectively removed under a rinsing or dissolving treatment with water or the like. After the rinsing treatment, solid residual materials or carbonized materials remain in the tank and reusable. Accordingly, the residual materials can be separated into respective materials which are different in characteristics by any separating means. The separated respective materials are dried and massed to be usable as fuel or the like. Additionally, liquid (such as water) used for the above rinsing treatment hardly contains no noxious substances and therefore can be discharged as it is to a river and the sea.

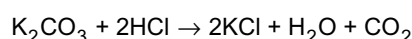
[0050] Next, a fourth embodiment of the noxious component or chlorine removal process according to the present invention will be discussed. In this embodiment, the noxious component or chlorine removal agent contains alkali metal hydrogen carbonate and/or alkali metal carbonate, i.e., at least one of potassium hydrogen carbonate (KHCO_3) and potassium carbonate (K_2CO_3), and used in the chlorine removal process for the treatable material which is polyvinyl chloride, polyvinylidene chloride, a synthetic resin containing chlorine, a rubber containing chlorine, and/or the like.

[0051] Discussion will be made on reactions carried out in the chlorine removal process of this embodiment. In case that potassium hydrogen carbonate (KHCO_3) is used as the chlorine removal agent, the following reaction is made between potassium hydrogen carbonate and hydrogen chloride (HCl):



[0052] Thus, potassium hydrogen carbonate reacts with hydrogen chloride thereby to form harmless potassium chloride and carbon dioxide gas.

[0053] In case of using potassium carbonate (K_2CO_3) as the chlorine removal agent, the following reaction is made between potassium carbonate and hydrogen chloride:



[0054] Thus, potassium carbonate reacts with hydrogen chloride thereby to form harmless potassium chloride, water and carbon dioxide gas.

[0055] As will be understood, in the heating process in which the reactions according to the above chemical reactions

are made, KCl is formed. KCl is a harmless chloride and can be effectively removed under a rinsing or dissolving treatment with water or the like. After the rinsing treatment, solid residual materials or carbonized materials remain in the tank and reusable. Accordingly, the residual materials can be separated into respective materials which are different in characteristics by any separating means. The separated respective materials are dried and massed to be usable as fuel or the like. Additionally, liquid (such as water) used for the above rinsing treatment hardly contains noxious substances and therefore can be discharged as it is to a river and the sea. More specifically, the residue taken out from the tank contains harmless chloride or potassium chloride (KCl). In order to extract the carbonized materials, the residue is put into a water tank containing water, and stirred for a predetermined time thereby dissolving sodium chloride. Subsequently, solid materials in the water tank are taken out from the water tank and then are subjected to a centrifugal dehydration to separate water content from the solid materials. The thus dehydrated solid materials are dried and massed. Water remaining in the water tank and the separated water content are drained through a separate draining and treatment means. It will be appreciated that carbon contents in the massed solid materials can be used as fuel while inorganic contents in the hardened mass can be used as materials for glass and cement. Further, as discussed above, the residue can be separated into respective materials which are different in characteristics by any separating means, upon which the separated respective materials are dried and massed to be effectively used as fuel or the like.

[0056] Next, a fifth embodiment of the noxious component removal process according to the present invention will be discussed. This noxious component removal process is for removing noxious component (such as chlorine and/or sulfur) from a treatable material (such as urban waste or trash, or industrial waste) containing the noxious component (such as chlorine and/or sulfur). The treatable material may contain polyvinyl chloride, polyvinylidene chloride, a synthetic resin containing chlorine, a rubber containing chlorine, so-called shredder dust (dust or trash produced by a paper-shredder), articles formed of polyvinyl chloride or polyvinylidene chloride, used tires, and formed polystyrene.

[0057] This embodiment will be discussed with reference to Fig. 1 illustrating a chlorine and sulfur removal system by which the process of this embodiment is carried out.

[0058] The chlorine and sulfur removal system comprises a mixing means or device 1 for mixing the treatable material (such as pulverized waste or trash) and the noxious component removal agent (such as sodium hydrogen carbonate) to form a mixture. A thermal treatment furnace 2 is formed cylindrical and rotatable. The mixture formed by the mixing device 1 is supplied into the furnace 2. The mixture may be formed by other means or devices than the mixing device 1. The thermal treatment furnace 2 is provided with a rotating transferring means or device (not shown) which is adapted to transfer the mixture under stirring. In the furnace 2, the mixture of the treatable material and the noxious component removal agent is heated in the low oxygen concentration atmosphere to accomplish thermal decomposition of the treatable material. The furnace 2 is provided with a heating coil 2 for heating the content of the furnace 2.

[0059] A residue treatment means or device 4 is provided to treat the residue (ash) formed upon heating the treatable material in the furnace 2. The residue is taken out of the furnace 2 and subjected to a solid-liquid separation. In this solid-liquid separation, the residue is rinsed with liquid such as water so that formed chloride and/or sulfite are separated and removed and then taken out from a liquid discharge section 4a. The residual solid such as metals and carbonized materials are taken out from a solid take-out section 4b. Emitted gas from the thermal treatment furnace 2 is introduced into an emitted gas treatment means or device 5. It will be understood that the emitted gas has been made harmless because the noxious components in the treatable material is removed under the action of the noxious component removal agent. A necessary treatment is made to the introduced emitted gas in the emitted gas treatment device 5. The treated gas from the gas treatment device 5 is then introduced into a gas recovery means or device 6 for recover the gas or into a secondary combustion means or device 7 to make secondary combustion of the gas to be discharged.

[0060] In this noxious component removal process using the above noxious component removal system, the treatable material containing the noxious component(s) and the noxious component removal agent (such as sodium hydrogen carbonate) are cast into the mixing device 1 and sufficiently mixed with each other, and then cast into the thermal treatment furnace 2. The treatable material may be pulverized prior to being cast, or pulverized simultaneously with mixing between the treatable material and the noxious component removal agent. The amount of the noxious component removal agent is within a range of from 5 to 30 % by weight relative to the treatable material. The thermal treatment or heating of the mixture in the thermal treatment furnace 2 is accomplished within temperature and time ranges to cover the temperature and time of generation of HCl gas and SO_x gas from the treatable material, the temperature (for example, 600 °C) and time (for example, 1 hour) having been determined under a previous investigation. These temperature and time are in relation to a condition (such as the size and the heating coil) of the thermal treatment furnace, the treatment amount of the treatable material, the treatment time of the thermal treatment of the treatable material, the treatment temperature of the thermal treatment of the treatable material. Therefore, the above temperature and time are required to be previously determined under a sufficient investigation and to accumulate the data to be taken for the temperature and time.

[0061] The thermal treatment in this process is under a heating condition for accomplishing dry distillation (or thermal decomposition) of the treatable material and therefore is not under another heating condition for accomplishing com-

bustion or incineration of the treatable material. Under this thermal treatment, noxious HCl gas and SO_x gas can be effectively react with each other upon contact of them, so that noxious HCl gas and SO_x gas are converted respectively into harmless chloride and sulfite.

[0062] In order to maintain this heating condition, a total reaction atmosphere or circumference inside the thermal treatment furnace can meet necessary conditions and be stable. For example, the stable low oxygen concentration atmosphere is formed inside the thermal treatment furnace. In other words, it is necessary to supply fresh air only around the treatable material during the heating or thermal treatment. If fresh air is supplied to around the treatable material, there is the possibility of combustion of the treatable material being initiated to make reaction stable. Otherwise, it has been experimentally confirmed that the heating condition can be maintained even by supplying fresh air into the thermal treatment furnace in such a manner that fresh air reaches whole the pulverized treatable material under a condition where unburned state of the treatable material is kept.

[0063] During the thermal treatment in the furnace, decomposition gas containing HCl gas and SO_x gas are generated, in which HCl and SO_x components immediately react with the noxious component removal agent or sodium hydrogen carbonate thereby to form harmless chloride (such as NaCl) and sulfite (Na₂SO₃), so that noxious HCl and SO_x are removed from the decomposition gas. The residue formed upon the thermal treatment of the treatable material contains no noxious HCl and SO_x. Thus, the decomposition gas and the residue can be simultaneously made harmless.

[0064] The residue is taken out through the residue treatment device 4 and rinsed with water or a solution thereby to separate the chloride and the sulfite from the residue, leaving solid residual material. The solid residual material contains useful metals which are effectively reusable.

[0065] Hereinafter, experiments for carrying out the noxious component removal process according to this embodiment will be discussed, in which comparison in experimental result is made between Examples (according to this embodiment) and Comparative Examples (not within the scope of the present invention). The experiments have revealed that the noxious component removal agent of this embodiment effectively react with HCl gas and SO_x gas so as to make harmless emitted gas and residue.

[0066] In the experiments, the noxious component removal process of this embodiment was carried out by using a refused derived fuel (referred hereinafter to as "RDF") as the treatable material. The RDF was formed from a waster or refuse and contains the following components:

garbage including refuse of meat, fish, bone, egg-shell, vegetable, fruit, and the like;
 plastic waste including polyethylene, polypropylene, polystyrene, polyvinylidene chloride, and the like;
 papers including tissue paper, advertisement bill, paper bag, paper box, and paper packing for drink, and the like;
 and
 combustibles including fiber matters such as fabric, wood piece, rubber, leather and the like.

[0067] As a result of analysis, it had been confirmed that RDF used in the experiments contained 60.173 % by weight of carbon (C), 16.277 % by weight of oxygen (O), 10.745 % by weight of silicon (Si), 7.045 % by weight of calcium (Ca), 3.314 % by weight of aluminum (Al), 0.888 % by weight of magnesium (Mg), 0.505 % by weight of phosphorus (P), 0.466 % by weight of chlorine (Cl), 0.331 % by weight of sulfur (S), and 0.155 % by weight of potassium (K), 0.101 % by weight of sodium (Na).

[0068] The experiments in connection with the present invention (Examples) used RDF (not subjected to thermal treatment or incineration) as the treatable material, whereas the experiments for the comparison purpose (Comparative Examples) used treated RDF (subjected to the thermal or incineration). For reference, in general, RDF whose main component is plastic contains 0.29 to 0.89 % by weight of chlorine component, and RDF whose main component is paper contains 0.2 % by weight of chlorine component. Additionally, it is general that the treated RDF contains about 1.0 % by weight of sulfur component.

[0069] As shown in Table 1, concerning Examples, 10 g of the chlorine removal agent (sodium hydrogen carbonate) was added to 40 g of the treatable material (crushed RDF) to form a mixture to be heated, in Example 5-1. The chlorine removal agent (sodium hydrogen carbonate) in an amount of 4g was added to 40 g of the treatable material (crushed RDF) to form a mixture to be heated, in Example 5-2. The chlorine removal agent (potassium hydrogen carbonate) in an amount of 3 g was added to 40 g of the treatable material (crushed RDF) to form a mixture to be heated, in Example 5-3. The chlorine removal agent (sodium carbonate and potassium carbonate) in an amount of 3 g was added to 20 g of the treatable material (crushed RDF) to form a mixture to be heated, in Example 5-4. The chlorine removal agent (sodium hydroxide) in an amount of 3 g was added to 20 g of the treatable material (crushed RDF) to form a mixture to be heated, in Example 5-5. The chlorine removal agent (potassium hydroxide) in an amount of 3 g was added to 20 g of the treatable material (crushed RDF) to form a mixture to be heated, in Example 5-6. The chlorine removal agent (sodium hydrogen carbonate) in an amount of 10 g was added to 40 g of the treatable material (RDF which had not been crushed and in the form of mass) to form a mixture to be heated, in Example 5-7. The chlorine removal agent was in the form of powder having an average particle size of 100 μm, in all Examples

[0070] Concerning Comparative Examples in which no noxious component removal agent was used, 40 g of the treated RDF which had been crushed was used as the treatable material in Comparative Example 5-1. The treated RDF which had been crushed was used in an amount of 20 g as the treatable material in Comparative Example 5-2. The treated RDF which had been not crushed and in the form of mass was used in an amount of 20 g as the treatable material in Comparative Example 5-3.

[0071] The experiment for each Example was conducted as follows: A predetermined amount of the treatable material was put into a tank or furnace, and then 20 g of the noxious component removal agent was added to and mixed with the treatable material in the tank to form the above-mentioned mixture. In the experiment for each Comparative Example, a predetermined amount of the treatable material was put into a tank or furnace. Then, the tank was tightly sealed so that the inside the tank was isolated from the outside air or atmospheric air in order that the mixture or only the treatable material was subjected to dry distillation upon heating. The thus sealed tank was stepwise heated with a heating coil, in which heating was made at eight temperature steps of 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C, 600 °C. In this heating step, the temperature at each of the eight steps was kept for 5 minutes, in which a concentration of HCl gas and a concentration of SO₂ in the tank was measured at each temperature rising time (at which the temperature was rising from one temperature step to the next temperature step) and at each temperature keeping time (at which the temperature at each temperature step was keeping). The temperature rising time is indicated as "Rising time" while the temperature keeping time is indicated as "Keeping time" in Tables 1 and 2. The tank was provided with a gas discharge pipe through which gas and pressure generated in the tank upon heating was discharged out of the tank. The measurement of the hydrogen chloride gas concentration was accomplished by using a detector tube according to JIS (Japanese Industrial Standard) - K0804, in which the detector tube was inserted into the gas discharge pipe to measure HCl and SO₂ gas concentrations. Results of HCl and SO₂ gas concentration measurement were shown in Tables 1 and 2. It is to be noted that ten times of the above experiment were repeated to obtain ten actual measured values of the hydrogen gas concentration for each Example and Comparative Example, in which the measured value (shown in Table 1) for each Example indicates the highest value in the measured values while the measured value (shown in Table 2) for each Comparative Example indicates the lowest value in the measured values. Additionally, "ND" in Tables 1 and 2 indicates the fact that no hydrogen chloride gas was detected in any of 10 times HCl and SO₂ gas concentration measurements to obtain the ten actual measured values. Further, manners of post-treatment for the noxious component removal agent were inspected and shown as "Post-treatment for chlorine removal agent" in Tables 1 and 2.

[0072] The experimental results will be discussed hereinafter with reference to Tables 1 and 2.

[0073] Regarding hydrogen chloride gas (HCl):

(a) In case that the treatable material was crushed, a slight amount of HCl gas was detected in Example 5-4; however, no HCl gas was detected in other Examples so that the noxious component removal agents were highly effective for suppressing generation of HCl gas. This HCl gas generation suppression effect was considerably high as compared with Comparative Examples 5-1 and 5-2.

(b) In case that the treatable material was not crushed and used in the form of mass, a slight amount of HCl gas was detected at the temperature steps of 350 to 450 °C in Example 5-7 as compared with the case that the treatable material was crushed; however, it was confirmed that the results in Example 5-7 was considerably good as compared with those in Comparative Examples.

Regarding sulfur oxide gas (SO₂):

[0074]

(a) In case that the treatable material was crushed, a slight amount of SO₂ gas was detected at the temperature steps of 400 to 450 °C in Examples 5-1 to 5-6; however, the results of Examples were very good as a whole so that the noxious component removal agents were highly effective for suppressing generation of SO₂ gas. This SO₂ gas generation suppression effect was considerably high as compared with Comparative Examples 5-1 and 5-2.

(b) In case that the treatable material was not crushed and used in the form of mass, a slight amount of SO₂ gas was detected at the temperature steps of 350 to 450 °C in Example 5-7 as compared with the case that the treatable material was crushed; however, it was confirmed that the results in Example 5-7 was considerably good as compared with those in Comparative Example 5-3.

[0075] As a result of the above experimental results and investigations, it has been confirmed that HCl and SO_x can be generally completely made harmless by using the noxious component removal agent containing the alkali metal compound which effectively reacts with HCl and SO_x to form harmless chloride and sulfite. Thus, the above reveals that if the noxious component removal agent is added to the treatable material to form the mixture to be subjected to

the thermal treatment, chlorine-containing gas and sulfur-containing gas generated from the treatable material can effectively become harmless.

[0076] It is to be noted that experiments similar to the above were conducted heating the treatable material at a higher temperature condition over 600 °C, which exhibited similar experimental results to the above. The temperature for heating the mixture of the treatable material and the chlorine removal agent may be selected according to form of facilities for accomplish the thermal treatment, time of the thermal treatment, amount of the treatable material and the like.

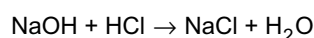
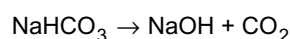
[0077] Subsequently, discussion will be made on mechanisms of reaction between the noxious component removal agent and noxious gas (chlorine-containing gas and sulfur-containing gas), realizing unexpected results in which both emitted gas and residue are made harmless.

(1) Regarding hydrogen chloride gas (HCl):

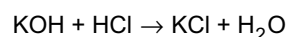
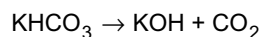
[0078] It was confirmed that sodium hydrogen carbonate (NaHCO_3), sodium carbonate (Na_2CO_3), sodium sesqui carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), natural soda (containing $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), sodium hydroxide (NaOH), potassium hydroxide (KOH), potassium carbonate (K_2CO_3), and potassium hydrogen carbonate (KHCO_3) can react with noxious HCl thereby to convert HCl into harmless chloride (NaCl and KCl) according to reaction formulae discussed before. It will be understood that sodium potassium carbonate and sodium carbonate hydrate can also react with noxious HCl similarly to the above.

[0079] Particularly in case of using the alkali metal hydrogen carbonate as the noxious component removal agent, the following tendency is predominant: First, CO_2 is separated at a temperature below a level (not lower than 250 °C) at which hydrogen chloride (HCl) is generated upon decomposition of the treatable material, forming NaOH or KOH. It is supposed that this forms an atmosphere in which reaction between NaOH or KOH and HCl is made smoothly. Here, the following reactions are made:

[0080] In case of sodium hydrogen carbonate,



[0081] In case of potassium hydrogen carbonate,



[0082] Thus, NaOH or KOH smoothly reacts with HCl thereby to newly form harmless chloride (NaCl, KCl).

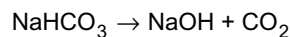
[0083] After the thermal treatment, the residue was left in the tank after the heating process had been completed. The residue was subjected to inspection, upon which it was detected that the residue did not contain noxious chlorine-containing gas component and contained harmless chloride (sodium chloride or potassium chloride). The residue was put into water and stirred for 10 minutes, in which the chloride was dissolved in water while carbonized materials remained. It was also detected that the carbonized materials did not contain chlorine-containing gas component.

[0084] Accordingly, chlorine-containing compound and chlorine component in the treatable material can be converted into sodium chloride (NaCl), potassium chloride (KCl), water (H_2O) and carbon dioxide gas (CO_2), and therefore hydrogen chloride forming part of a source of dioxin cannot be formed thereby realizing the unexpected result of making both emitted gas and residue harmless.

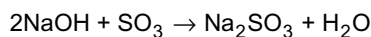
(2) Regarding sulfur oxide gas (SO_x):

[0085] It was confirmed that the noxious component removal agent reacts with noxious SO_x thereby to convert SO_x into harmless sulfite as follows:

[0086] In case that sodium hydrogen carbonate is used as the noxious component removal agent,

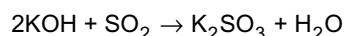
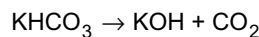


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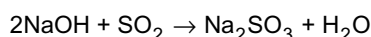


[0087] In case that potassium hydrogen carbonate is used as the noxious component removal agent,

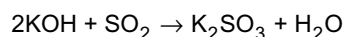
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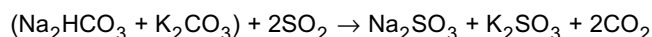
15 **[0088]** In case that sodium hydroxide is used as the noxious component removal agent,



20 **[0089]** In case that potassium hydroxide is used as the noxious component removal agent,

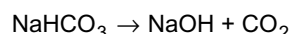


25 **[0090]** In case that sodium potassium carbonate is used as the noxious component removal agent,

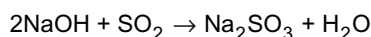


30 **[0091]** Particularly in case of using the alkali metal hydrogen carbonate as the noxious component removal agent, the following tendency is predominant: First, CO_2 is separated at a temperature below a level (not lower than 300 °C) at which sulfur oxide (SO_2) is generated upon decomposition of the treatable material, forming NaOH or KOH. It is supposed that this forms an atmosphere in which reaction between NaOH or KOH and SO_2 is made smoothly. Here, the following reactions are made:

35 **[0092]** In case of sodium hydrogen carbonate,

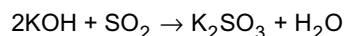
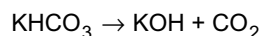


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[0093] In case of potassium hydrogen carbonate,

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[0094] Thus, NaOH or KOH smoothly reacts with SO_2 thereby to newly form harmless sulfite (Na_2SO_3 , K_2SO_3).

[0095] It was confirmed sodium carbonate (Na_2CO_3), sodium sesqui carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), natural soda (containing $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), potassium carbonate (K_2CO_3), and sodium carbonate hydrate can react with noxious SO_2 thereby to convert SO_2 into harmless chloride sulfite (Na_2SO_3 , K_2SO_3) according to reaction formulae discussed hereinbefore.

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[0096] Upon the above-mentioned inspection of the residue, it was detected that the residue did not contain noxious sulfur-containing gas (SO_x gas) component and contained harmless sulfite (Na_2SO_3 , K_2SO_3). The residue was put into water and stirred for 10 minutes, in which the alkali metal sulfite was dissolved in water while carbonized materials

remained. It was also detected that the carbonized materials did not contain sulfur-containing (SOx) gas component.

[0097] Accordingly, sulfur-containing compound and sulfur component in the treatable material can be converted into sodium sulfite (Na_2SO_3) in powder form, and potassium sulfite (K_2SO_3) in powder form, water (H_2O) and carbon dioxide gas (CO_2), and therefore SOx gas can be prevented from generation thus realizing the unexpected result of making both emitted gas and residue harmless.

[0098] It will be appreciated that, in this embodiment, the noxious component removal agent contains at least one of alkali metal carbonate, alkali metal hydrogen carbonate, and alkali metal hydroxide, i.e., at least one of sodium hydrogen carbonate (NaHCO_3), sodium carbonate (Na_2CO_3), sodium sesqui carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), natural soda (containing $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), sodium hydroxide (NaOH), potassium hydroxide (KOH), potassium carbonate (K_2CO_3), and potassium hydrogen carbonate (KHCO_3), potassium sodium carbonate ($\text{KNaCO}_3 \cdot 6\text{H}_2\text{O}$). As will be understood, in the heating process in which the reactions according to the above chemical reactions are made, noxious hydrogen chloride and/or sulfur oxide are converted into harmless chloride (NaCl , KCl) and/or sulfite (Na_2SO_3 , K_2SO_3), thereby making it possible to remove noxious components (hydrogen chloride and/or sulfur oxide) from the decomposition gas generated from the treatable material upon heating. Thus, the decomposition gas or emitted gas from the furnace can be effectively made harmless. The chloride and/or sulfite form part of the residue and can be effectively removed under a rinsing or dissolving treatment with water or the like. After the rinsing treatment, solid residual materials or carbonized materials remain in the tank and reusable. Accordingly, the residual materials can be separated into respective materials which are different in characteristics by any separating means. The separated respective materials are dried and massed to be usable as fuel or the like. Additionally, liquid (such as water) used for the above rinsing treatment hardly contains no noxious substances and therefore can be discharged as it is to a river and the sea.

TABLE 1

Temp. °C	Treatable material	Example 5-1		Example 5-2		Example 5-3		Example 5-4		Example 5-5		Example 5-6		Example 5-7	
		RDF Crushed 40g	NaHCO ₃ 10g	RDF Crushed 40g	NaHCO ₃ 4g	RDF Crushed 20g	KHCO ₃ 3g	RDF Crushed 20g	Na ₂ CO ₃ K ₂ CO ₃ 3g	RDF Crushed 20g	NaOH 3g	RDF Crushed 20g	KOH 3g	RDF Mass 40g	NaHCO ₃ 10g
	Noxious comp. removable material														
	Measuring time	HCl concentration (not higher than)	SO ₂ concentration (not higher than)	HCl concentration (not higher than)	SO ₂ concentration (not higher than)	HCl concentration (not higher than)	SO ₂ concentration (not higher than)	HCl concentration (not higher than)	SO ₂ concentration (not higher than)	HCl concentration (not higher than)	SO ₂ concentration (not higher than)	HCl concentration (not higher than)	SO ₂ concentration (not higher than)	HCl concentration (not higher than)	SO ₂ concentration (not higher than)
250	Rising time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
300	Rising time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
350	Rising time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
400	Rising time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
450	Rising time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
500	Rising time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
550	Rising time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
600	Rising time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	Post-treatment for noxious comp. removal agent	Soluble in water		Soluble in water		Soluble in water		Soluble in water		Soluble in water		Soluble in water		Soluble in water	

TABLE 2

		Comparative Example 5-1		Comparative Example 5-2		Comparative Example 5-3	
Treatable material		Treated RDF Crushed 40g		Treated RDF Crushed 20g		Treated RDF Mass 40g	
Noxious comp. removal agent		—		—		—	
Temp. °C	Measuring time	HCl concent- ration (not lower than)	SO ₂ concent- ration (not lower than)	HCl concent- ration (not lower than)	SO ₂ concent- ration (not lower than)	HCl concent- ration (not lower than)	SO ₂ concent- ration (not lower than)
250	Rising time	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND
300	Rising time	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND
350	Rising time	ND	7ppm	ND	20ppm	2ppm	6ppm
	Keeping time	16ppm	40ppm	13ppm	17ppm	35ppm	60ppm
400	Rising time	70ppm	35ppm	30ppm	13ppm	1000ppm	60ppm
	Keeping time	60ppm	30ppm	3ppm	7ppm	130ppm	20ppm
450	Rising time	10ppm	7ppm	1ppm	4ppm	10ppm	10ppm
	Keeping time	2ppm	3ppm	ND	ND	ND	5ppm
500	Rising time	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND
550	Rising time	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND
600	Rising time	ND	ND	ND	ND	ND	ND
	Keeping time	ND	ND	ND	ND	ND	ND
Post-treatment for noxious comp. removal agent		—		—		—	

Claims

1. A process for removing at least one of chlorine and sulfur from a treatable material containing at least one of chlorine and sulfur, comprising the following steps in the sequence set forth:

mixing the treatable material and a chlorine and sulfur removal agent to form a mixture, said chlorine and sulfur removal agent containing at least one compound selected from the group consisting of a sodium compound and a potassium compound; and

supplying the mixture into a furnace;
stirring and

heating said mixture in a low oxygen concentration atmosphere in the furnace to thermally decompose the treatable material to generate at least one of a chlorine-containing substance and a sulfur-containing substance

and cause at least one of the chlorine-containing substance and the sulfur-containing substance to contact and react with said chlorine and sulfur removal agent to form at least one of harmless chloride and sulfite.

2. A process according to claim 1, wherein chlorine is removed from a treatable material containing chlorine.
3. A process according to claim 1 or 2, wherein said removal agent contains at least one compound selected from the group consisting of sodium and potassium carbonate, hydrogen carbonate, and hydroxide.
4. A process according to claim 1 or 2, wherein said removal agent contains at least one compound selected from the group consisting of sodium hydrogen carbonate, sodium carbonate, sodium sesqui carbonate, natural soda, sodium hydroxide, potassium hydroxide, potassium carbonate, potassium hydrogen carbonate, and potassium sodium carbonate.
5. A process according to claim 2, wherein the heating step includes the step of heating said mixture in a furnace which is substantially sealed so as to prevent fresh air from being supplied into said furnace, in which a pressure in said furnace leaking out of said furnace.
6. A process according to claim 2, wherein the heating step includes the step of heating said mixture to cause said treatable material to make its dry distillation.
7. A process according to claim 2, wherein said removal agent is in form of at least one selected from the group consisting of mass, plate, porous body, particle, solution and suspension.
8. A process according to claim 2, wherein said treatable material is at least one selected from the group consisting of polyvinyl chloride, polyvinylidene chloride, a synthetic resin containing chlorine, and a rubber containing chlorine.
9. A process according to claim 2, wherein said removal agent in said mixing step is in an amount ranging from 0.05 to 10% by weight relative to the treatable material at a time before said mixing step.
10. A process according to claim 2, wherein said removal agent in said mixing step is in an amount ranging from 10 to 70% weight relative to the treatable material in case that the treatable material is at least one selected from the group consisting of polyvinyl chloride, polyvinylidene chloride, a synthetic resin containing chlorine, and a rubber containing chlorine.
11. A process according to claim 2, wherein said removal agent in said mixing step is in an amount of not less than a chemical equivalent of chlorine to be generated from the treatable material.
12. A process according to claim 2, further comprising the step of adding said removal agent to said mixture in said heating step.
13. A process according to claim 12, wherein the adding step includes adding said removal agent to said mixture before a temperature of the treatable material reaches a level at which a thermal decomposition of the treatable material occurs.
14. A process according to claim 12, wherein the adding step includes adding said removal agent to said mixture after a temperature of the treatable material reaches a level at which a thermal decomposition of the treatable material occurs.
15. A process according to claim 2, further comprising supplying said removal agent to the treatable material in a furnace by at least one measure selected from the group consisting of casting and spraying.
16. A process according to claim 2, wherein said heating step includes heating the treatable material at a temperature ranging from 200 to 1000 °C.
17. A system for removing at least one of chlorine and sulfur from a treatable material containing at least one of chlorine and sulfur, comprising:

a device for mixing the treatable material and a chlorine and sulfur removal agent to form a mixture, said

chlorine and sulfur removal agent containing at least one compound selected from the group consisting of a sodium compound and a potassium compound;

a furnace into which said mixture of the treatable material and said chlorine and sulfur removal agent is supplied, said furnace being adapted to form therein a low oxygen concentration atmosphere and being provided with a rotating transferring means; and

a heating device for heating said mixture in the low oxygen concentration atmosphere in said furnace to thermally decompose the treatable material so as to accomplish dry distillation of said treatable material, in which said mixture generates at least one of a chlorine-containing substance and a sulfur-containing substance and cause at least one of the chlorine-containing substance and the sulfur-containing substance to contact and react with said chlorine and sulfur removal agent to form at least one of harmless chloride and sulfite.

18. A system according to claim 17, wherein said chlorine and sulfur removal agent contains at least one compound selected from the group consisting of sodium and potassium carbonate, hydrogen carbonate, and hydroxide.

19. A system according to claim 17, wherein said chlorine and sulfur removal agent contains at least one compound selected from the group consisting of sodium hydrogen carbonate, sodium carbonate, sodium sesqui carbonate, natural soda, sodium hydroxide, potassium hydroxide, potassium carbonate, potassium hydrogen carbonate, and potassium sodium carbonate.

Patentansprüche

1. Verfahren zum Entfernen von Chlor oder Schwefel oder beiden aus einem zu behandelnden Material, das Chlor oder Schwefel oder beide enthält, wobei das Verfahren die folgenden Schritte in der angegebenen Reihenfolge aufweist:

Mischen des zu behandelnden Materials und eines Mittels zum Entfernen von Chlor und Schwefel unter Bildung einer Mischung, wobei das Mittel zum Entfernen von Chlor und Schwefel wenigstens eine Verbindung aus der Gruppe enthält, die aus einer Natriumverbindung und einer Kaliumverbindung besteht; und

Zuführen der Mischung in einen Ofen;

Rühren und Erhitzen der Mischung in einer Atmosphäre mit niedriger Sauerstoffkonzentration in dem Ofen, um das zu behandelnde Material thermisch zu zersetzen, um eine chlor- oder schwefelhaltige Substanz oder beide zu erzeugen und die chlor- oder schwefelhaltige Substanz oder beide mit dem Mittel zum Entfernen von Chlor und Schwefel in Kontakt kommen und reagieren zu lassen, um unschädliches Chlorid oder Sulfit oder beides zu bilden.

2. Verfahren nach Anspruch 1, bei dem Chlor aus einem zu behandelnden, chlorhaltigen Material entfernt wird.

3. Verfahren nach Anspruch 1 oder 2, bei dem das Mittel zum Entfernen wenigstens eine Verbindung aus der Gruppe enthält, die aus Natrium- und Kaliumcarbonat, -hydrogencarbonat und -hydroxid besteht.

4. Verfahren nach Anspruch 1 oder 2, bei dem das Mittel zum Entfernen wenigstens eine Verbindung aus der Gruppe enthält, die aus Natriumhydrogencarbonat, Natriumcarbonat, Natriumsesquicarbonat, Natursoda, Natriumhydroxid, Kaliumhydroxid, Kaliumcarbonat, Kaliumhydrogencarbonat und Kaliumnatriumcarbonat besteht.

5. Verfahren nach Anspruch 2, bei dem der Heizschritt den Schritt des Erhitzens der Mischung in einem Ofen einschließt, der im wesentlichen abgedichtet ist, um zu verhindern, daß Frischluft dem Ofen zugeführt wird, indem ein Druck im Ofen aus dem Ofen austritt.

6. Verfahren nach Anspruch 2, bei dem der Heizschritt den Schritt des Erhitzens der Mischung einschließt, um das zu behandelnde Material zu dessen Trockendestillation zu veranlassen.

7. Verfahren nach Anspruch 2, bei dem das Material zum Entfernen wenigstens eine der Formen aus der Gruppe aufweist, die aus Masse, Platte, porösem Körper, Teilchen, Lösung und Suspension besteht.

8. Verfahren nach Anspruch 2, bei dem das zu behandelnde Material wenigstens eines aus der Gruppe ist, die aus Polyvinylchlorid, Polyvinylidenchlorid, einem synthetischen, chlorhaltigen Harz und einem chlorhaltigen Kautschuk besteht.

9. Verfahren nach Anspruch 2, bei dem das Material zum Entfernen in dem Mischschritt in einer Menge im Bereich von 0,05 bis 10 Gew.-% vorliegt, bezogen auf das zu behandelnde Material zum Zeitpunkt vor dem Mischschritt.

10. Verfahren nach Anspruch 2, bei dem das Mittel zum Entfernen in dem Mischschritt in einer Menge im Bereich von 10 bis 70 Gew.-% vorliegt, bezogen auf das zu behandelnde Material, sofern das zu behandelnde Material wenigstens eines aus der Gruppe ist, die aus Polyvinylchlorid, Polyvinylidenchlorid, einem synthetischen, chlorhaltigen Harz und einem chlorhaltigen Kautschuk besteht.

11. Verfahren nach Anspruch 2, bei dem das Mittel zum Entfernen in dem Mischschritt in einer Menge nicht unter einem chemischen Äquivalent des Chlors vorliegt, das aus dem zu behandelnden Material freizusetzen ist.

12. Verfahren nach Anspruch 2, das außerdem den Schritt der Zugabe des Mittels zum Entfernen zu der Mischung in dem Heizschritt aufweist.

13. Verfahren nach Anspruch 12, bei dem die Zugabe des Mittels zum Entfernen zu der Mischung erfolgt, bevor die Temperatur des zu behandelnden Materials eine Höhe erreicht, bei der eine thermische Zersetzung des zu behandelnden Materials stattfindet.

14. Verfahren nach Anspruch 12, bei dem die Zugabe des Mittels zum Entfernen zu der Mischung erfolgt, nachdem die Temperatur des zu behandelnden Materials eine Höhe erreicht hat, bei der eine thermische Zersetzung des zu behandelnden Materials stattfindet.

15. Verfahren nach Anspruch 2, bei dem außerdem die Zuführung des Mittels zum Entfernen zu dem zu behandelnden Material in einem Ofen durch Gießen und/oder Sprühen erfolgt.

16. Verfahren nach Anspruch 2, bei dem im Heizschritt das Erhitzen des zu behandelnden Materials auf eine Temperatur im Bereich von 200 bis 1000°C erfolgt.

17. System zum Entfernen von Chlor oder Schwefel oder beiden aus einem zu behandelnden Material, das Chlor oder Schwefel oder beide enthält, mit:

einer Vorrichtung zum Mischen des zu behandelnden Materials und eines Mittels zum Entfernen von Chlor und Schwefel unter Bildung einer Mischung, wobei das Mittel zum Entfernen von Chlor und Schwefel wenigstens eine Verbindung aus der Gruppe enthält, die aus einer Natriumverbindung und einer Kaliumverbindung besteht;

einem Ofen, dem die Mischung aus dem zu behandelnden Material und dem Mittel zum Entfernen von Chlor und Schwefel zugeführt wird, wobei der Ofen so angepaßt ist, um eine Atmosphäre mit niedriger Sauerstoffkonzentration darin zu bilden, und mit einem rotierenden Transportmittel ausgestattet ist; und

einer Heizeinrichtung zum Heizen der Mischung in der Atmosphäre mit niedriger Sauerstoffkonzentration in dem Ofen, um das zu behandelnde Material thermisch zu zersetzen, so daß eine Trockendestillation des zu behandelnden Materials durchgeführt wird, bei der die Mischung eine chlor- oder schwefelhaltige Substanz oder beide erzeugt und die chlor- oder schwefelhaltige Substanz oder beide mit dem Mittel zum Entfernen von Chlor und Schwefel in Kontakt und zur Reaktion gebracht wird, um unschädliches Chlorid oder Sulfit oder beides zu bilden.

18. System nach Anspruch 17, bei dem das Mittel zum Entfernen von Chlor und Schwefel wenigstens eine Verbindung aus der Gruppe enthält, die aus Natrium- und Kaliumcarbonat, -hydrogencarbonat und -hydroxid besteht.

19. System nach Anspruch 17, bei dem das Mittel zum Entfernen von Chlor und Schwefel wenigstens eine Verbindung aus der Gruppe enthält, die aus Natriumhydrogencarbonat, Natriumcarbonat, Natriumsesquicarbonat, Natursoda, Natriumhydroxid, Kaliumhydroxid, Kaliumcarbonat, Kaliumhydrogencarbonat und Kaliumnatriumcarbonat besteht.

Revendications

1. Procédé permettant d'éliminer le soufre et/ou le chlore d'un matériau à traiter contenant du soufre et/ou du chlore, lequel procédé comporte les étapes suivantes, effectuées dans l'ordre indiqué :

- mélanger, pour en faire un mélange, le matériau à traiter et un agent d'élimination de chlore et de soufre, lequel agent contient au moins un composé choisi dans l'ensemble constitué par les composés du sodium et les composés du potassium ;
- envoyer le mélange dans un four ;
- et brasser et chauffer ledit mélange dans le four, dans une atmosphère à faible teneur en oxygène, pour provoquer la décomposition thermique du matériau à traiter et la formation d'une substance chlorée et/ou d'une substance soufrée, puis faire que cette substance chlorée et/ou cette substance soufrée entrent en contact avec ledit agent d'élimination de chlore et de soufre et réagissent avec celui-ci, pour former un chlorure et/ou un sulfite non nocif(s).

2. Procédé conforme à la revendication 1, par lequel on élimine le chlore d'un matériau à traiter contenant du chlore.

3. Procédé conforme à la revendication 1 ou 2, dans lequel ledit agent d'élimination contient au moins un composé choisi dans l'ensemble que constituent les carbonates, hydrogénocarbonates et hydroxydes de sodium et/ou de potassium.

4. Procédé conforme à la revendication 1 ou 2, dans lequel ledit agent d'élimination contient au moins un composé choisi dans l'ensemble que constituent l'hydrogénocarbonate de sodium, le carbonate de sodium, le sesquicarbonate de sodium, la soude naturelle, l'hydroxyde de sodium, l'hydroxyde de potassium, le carbonate de potassium, l'hydrogénocarbonate de potassium, et le carbonate de sodium et de potassium.

5. Procédé conforme à la revendication 2, dans lequel ladite étape de chauffage comporte le fait de chauffer ledit mélange dans un four qui est pratiquement fermé de manière à empêcher l'air frais de pénétrer dans le four, la pression qui règne à l'intérieur du four engendrant des fuites vers l'extérieur de ce four.

6. Procédé conforme à la revendication 2, dans lequel ladite étape de chauffage comporte le fait de chauffer ledit mélange de manière à provoquer la distillation sèche du matériau à traiter.

7. Procédé conforme à la revendication 2, dans lequel ledit agent d'élimination se présente sous au moins une forme choisie parmi les suivantes : masse, plaque, corps poreux, particules, solution et suspension.

8. Procédé conforme à la revendication 2, dans lequel ledit matériau à traiter est au moins un matériau choisi parmi les suivants : poly(chlorure de vinyle), poly(chlorure de vinylidène), résines synthétiques chlorées et caoutchoucs chlorés.

9. Procédé conforme à la revendication 2, dans lequel, dans ladite étape de formation d'un mélange, on ajoute ledit agent d'élimination en une quantité représentant de 0,05 à 10 % du poids qu'a le matériau à traiter avant cette étape de formation d'un mélange.

10. Procédé conforme à la revendication 2, dans lequel, dans ladite étape de formation d'un mélange, on ajoute ledit agent d'élimination en une quantité représentant de 10 à 70 % du poids du matériau à traiter, dans le cas où ledit matériau à traiter est au moins un matériau choisi parmi les suivants : poly(chlorure de vinyle), poly(chlorure de vinylidène), résines synthétiques chlorées et caoutchoucs chlorés.

11. Procédé conforme à la revendication 2, dans lequel, dans ladite étape de formation d'un mélange, on ajoute ledit agent d'élimination en une quantité représentant au moins un équivalent chimique par rapport au chlore qui peut se dégager du matériau à traiter.

12. Procédé conforme à la revendication 2, qui comporte en outre le fait de rajouter dudit agent d'élimination audit mélange, au cours de ladite étape de chauffage.

13. Procédé conforme à la revendication 12, dans lequel ladite étape d'addition comporte le fait de rajouter dudit agent d'élimination audit mélange avant que la température du matériau à traiter atteigne une valeur à laquelle se produit la décomposition thermique du matériau à traiter.

14. Procédé conforme à la revendication 12, dans lequel ladite étape d'addition comporte le fait de rajouter dudit agent d'élimination audit mélange après que la température du matériau à traiter a atteint une valeur à laquelle se produit la décomposition thermique du matériau à traiter.

15. Procédé conforme à la revendication 2, qui comporte en outre le fait d'appliquer dudit agent d'élimination sur ledit matériau à traiter, dans un four, en opérant selon au moins une méthode choisie parmi l'enduction par coulée et la projection par pulvérisation.

16. Procédé conforme à la revendication 2, dans lequel ladite étape de chauffage comporte le fait de chauffer le matériau à traiter à une température valant de 200 à 1000 °C.

17. Système permettant d'éliminer le soufre et/ou le chlore d'un matériau à traiter contenant du soufre et/ou du chlore, lequel système comporte

- un dispositif servant à mélanger, pour en faire un mélange, le matériau à traiter et un agent d'élimination de chlore et de soufre, lequel agent contient au moins un composé choisi dans l'ensemble constitué par les composés du sodium et les composés du potassium ;
- un four dans lequel est envoyé ledit mélange du matériau à traiter et dudit agent d'élimination de chlore et de soufre, ledit four étant adapté en vue de la constitution, en son intérieur, d'une atmosphère à faible teneur en oxygène, et muni d'un moyen rotatif de transfert de matière ;
- et un dispositif de chauffage servant à chauffer ledit mélange dans ledit four, dans ladite atmosphère à faible teneur en oxygène, pour provoquer la décomposition thermique du matériau à traiter de manière à ce que s'accomplisse la distillation sèche de ce matériau à traiter, pendant laquelle se dégagent dudit mélange une substance chlorée et/ou une substance soufrée, puis à ce que cette substance chlorée et/ou cette substance soufrée entrent en contact avec ledit agent d'élimination de chlore et de soufre et réagissent avec celui-ci, pour former un chlorure et/ou un sulfite non nocif(s).

18. Système conforme à la revendication 17, dans lequel ledit agent d'élimination de chlore et de soufre contient au moins un composé choisi dans l'ensemble que constituent les carbonates, hydrogénocarbonates et hydroxydes de sodium et/ou de potassium.

19. Système conforme à la revendication 17, dans lequel ledit agent d'élimination de chlore et de soufre contient au moins un composé choisi dans l'ensemble que constituent l'hydrogénocarbonate de sodium, le carbonate de sodium, le sesquicarbonate de sodium, la soude naturelle, l'hydroxyde de sodium, l'hydroxyde de potassium, le carbonate de potassium, l'hydrogénocarbonate de potassium, et le carbonate de sodium et de potassium.

FIG.1

