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(54) METHOD FOR ELIMINATING RADIOACTIVE CESIUM AND METHOD FOR PRODUCING BURNED PRODUCT

(57) Provided is a method of easily and efficiently removing radioactive cesium from a waste contaminated with radioactive cesium. The method of removing radioactive cesium includes a heating step of heating a waste contaminated with radioactive cesium and a CaO source and/or a MgO source at a temperature of from 1,200 to 1,350°C to volatilize the radioactive cesium in the waste. In the heating step, the kinds and the blending ratios of the waste, the CaO source, and the MgO source are set so that the masses of CaO, MgO, and SiO_2 satisfy the equation: $(CaO+1.39\times MgO)/SiO_2)=1.0$ to 2.5 (in the equation, CaO, MgO, and SiO_2 represent the mass of calcium in terms of an oxide, the mass of magnesium in terms of an oxide, and the mass of silicon in terms of an oxide, respectively).

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Description

Technical Field

[0001] The present invention relates to a method of removing radioactive cesium from a waste contaminated with radioactive cesium, and to a method of producing a harmless burned product (for example, a cement admixture, an aggregate, and a civil work material) by using a waste contaminated with radioactive cesium as a raw material.

Background Art

[0002] Radioactive cesium released from a nuclear power plant to an external environment by a large accident is disadvantageously contained in a waste or soil in some cases. Radioactive cesium (i.e. cesium 137) is often required to be removed from the waste or the like, because radioactive cesium has a half-life period of 30 years and may adversely affect a human body over a long period of time.

[0003] As a method of removing radioactive cesium, for example, there is disclosed a method of treating a radioactive waste which involves melting a radioactive waste in a form of a nitrate salt through electromagnetic induction heating in a cooled container having a slit and equipped with an energizing coil wound around outside the container, collecting a metal oxide generated through decomposition of the nitrate salt on an inner circumference of the container and a reduced platinum group metal in a central portion of the container through electromagnetic pinch force, followed by cooling and solidification, and then recovering a generated solidified mate rial, wherein the method involves separating and recovering a long-lived nuclide such as cesium volatilized from the radioactive waste during the electromagnetic induction heating (see Patent Literature 1).

[0004] However, the method disclosed in Patent Literature 1 is not targeted at radioactive cesium released to an external environment by an accident, but at a radioactive waste generated in a limited region of a nuclear power plant or the like. Therefore, the method is not suitable for treatment of an enormous amount of contaminated soil or the like, and there are problems of a complex and expensive apparatus and high cost.

Citation List

Patent Literature

[0005] [Patent Literature 1] JP 05-157897 A

Summary of Invention

Problems to be Solved by the Invention

[0006] An object of the present invention is to provide a method of removing easily and efficiently radioactive cesium from a waste contaminated with radioactive cesium. Another obj ect of the present invention is to provide a method of producing a harmless burned product (for example, a cement admixture, an aggregate, and a civil work material) by using a waste contaminated with radioactive cesium as a raw material.

Means for Solving the Problems

[0007] In order to achieve the above-mentioned objects, the inventors of the present invention have made intensive studies. As a result, the inventors have found that the objects can be achieved by heating a waste contaminated with radioactive cesium and a CaO source and/or a MgO source at specific blending ratios. Thus, the present invention has been completed.

[0008] That is, the present invention provides the following items [1] to [9].

[1] A method of removing radioactive cesium which includes a heating step of heating a waste contaminated with radioactive cesium and a CaO source and/or a MgO source at a temperature of from 1,200 to 1, 350 °C to volatilize the radioactive cesium in the waste, wherein in the heating step, the kinds and the blending ratios of the waste, the CaO source, and the MgO source are set so that the masses (i.e. weights) of CaO, MgO, and SiO_2 satisfy the following equation (1) :

$$((CaO+1.39\times MgO)/SiO_2)=1.0\text{ to }2.5 \qquad (1)$$

wherein CaO, MgO, and SiO_2 in the equation (1) represent the mass (i.e. weight) of calcium in terms of an oxide (i.e. CaO), the mass of magnesium in terms of an oxide (i.e. MgO), and the mass of silicon in terms of an oxide (i.e. SiO_2), respectively.

[2] A method of removing radioactive cesium according to the aforesaid item [1], wherein the heating step further includes using a chloride.

[3] A method of removing radioactive cesium according to the aforesaid item [1] or [2], wherein the heating in the heating step is performed in a reducing (i.e. reductive) atmosphere.

[4] A method of producing a burned product which includes a heating step of heating a waste contaminated with radioactive cesium and a CaO source and/or a MgO source at a temperature of from 1,200 to 1,350°C to volatilize the radioactive cesium in the waste and thereby produce a burned product, wherein in the heating step, the kinds and the blending ratios of the waste, the CaO source, and the MgO source are set so that the masses of CaO, MgO, and SiO_2 satisfy the following equation (1):

$$((CaO+1.39\times MgO)/SiO_2)=1.0\text{ to }2.5 \qquad (1)$$

wherein CaO, MgO, and SiO_2 in the equation (1) represent the mass of calcium in terms of an oxide, the mass of magnesium in terms of an oxide, and the mass of silicon in terms of an oxide, respectively.

[5] A method of producing a burned product according to the aforesaid item [4], wherein the heating in the heating step is performed in a reducing atmosphere.

[6] A method of producing a burned product according to the aforesaid item [4] or [5], which further includes a mixing step of mixing the burned product obtained by the heating step with at least one kind selected from the group consisting of a reducing agent and an adsorbent.

[7] A cement admixture which is obtained by grinding a burned product obtained by the method of producing a burned product according to any one of the aforesaid items [4] to [6].

[8] An aggregate which is made of a burned product obtained by the method of producing a burned product according to any one of the aforesaid items [4] to [6].

[9] A civil work material which is made of a burned product obtained by the method of producing a burned product according to any one of the aforesaid items [4] to [6].

Advantageous Effects of the Invention

[0009] According to the method of removing radioactive cesium of the present invention, radioactive cesium can be removed from a waste contaminated with radioactive cesium easily and efficiently. Thus, the volume of a radioactive waste can be reduced.

[0010] Also, according to the method of producing a burned product of the present invention, a harmless burned product, from which radioactive cesium has been removed, can be obtained. The burned product can be used as a cement admixture or an aggregate which is for forming concrete for reconstruction (for example, a levee, a breakwater, a wave-dissipating block, or the like) required in a large amount in the future. This enables saving of natural resources. The burned product can be utilized as a civil work material (i.e. an earthmoving material) such as a backfill material for a land from which soil has been removed, or the like.

Embodiments for Carrying Out the Invention

[0011] The present invention is hereinafter described in detail.

[0012] A method of removing radioactive cesium of the present invention includes a heating step of heating a waste contaminated with radioactive cesium and a CaO source and/or a MgO source at a temperature of from 1,200 to 1,350°C to volatilize the radioactive cesium in the waste, wherein in the heating step, the kinds and the blending ratios of the waste, the CaO source, and the MgO source are set so that the masses of CaO, MgO, and SiO_2 satisfy the following equation (1):

$$((CaO+1.39\times MgO)/SiO_2)=1.0\text{ to }2.5 \qquad (1)$$

wherein CaO, MgO, and SiO_2 represent the mass of calcium in terms of an oxide, the mass of magnesium in terms of an oxide, and the mass of silicon in terms of an oxide, respectively.

[0013] The object substance to be treated by the present invention is a waste contaminated with radioactive cesium.

[0014] The waste contaminated with radioactive cesium herein refers to a waste containing radioactive cesium. Examples of a waste containing radioactive cesium include: a general waste such as soil, dried sewage sludge powder, municipal refuse incineration ash, molten slag derived from refuse, a seashell, and a plant or wood; an industrial waste such as sewage sludge, sewage slag, sludge from water purification, and construction sludge; and a disaster waste such as rubble. Those wastes may be used alone or two or more kinds thereof may be used in combination. One (i.e. an intermediate treatment product) having radioactive cesium condensed therein obtained by preliminarily removing a portion containing little radioactive cesium (for example, sand or stone in the case of soil) is also included in the concept of the "waste contaminated with radioactive cesium" in the present invention.

[0015] Examples of the CaO source include calciumcarbonate, limestone, quick lime (i.e. burnt lime), slaked lime (i.e. hydrated lime), dolomite, and blast furnace slag. Examples of the MgO source include magnesium carbonate, magnesium hydroxide, dolomite, serpentine, and ferronickel slag. Those exemplified sources maybe used alone, or two or more kinds thereof may be used in combination.

[0016] In the present invention, both of or any one of the CaO source and the MgO source may be used. In view of volatilization property of radioactive cesium, it is preferred to use only the CaO source.

[0017] The CaO source and the MgO source are preferably used in a powder form (i.e. in a powdery state) obtained through grinding.

[0018] In the present invention, the radioactive cesium means cesium 134 and cesium 137, which are radioactive cesium isotopes. Those radioactive cesium isotopes are radioactive substances to be released from a nuclear power plant to the external environment by an accident, and have a half-life period of about 2 years and about 30 years, respectively.

[0019] The radioactive cesium to be removed in the present invention is one released from a nuclear power plant having an accident to the external environment in the form of cesium iodide or the like together with radioactive iodine, and then flew down from the sky to the surface of the ground. Cesium iodide has a boiling point of 1,200°C or more, and hence has a property of being less volatile as compared to elemental cesium having a boiling point of about 700°C. Besides, the radioactive cesium flew down to the surface of the ground may be trapped in a clay mineral contained in soil in a state of being hardly separated from the soil or in an altered form. The radioactive cesium attached to a disaster waste such as rubble or flew down to the surface of the ground is allowed to flow by rain and generates sewage sludge or the like containing radioactive cesium at a high concentration thorough condensation in the course of sewage treatment. A plant or wood may be radioactively contaminated through absorption of the radioactive cesium contained in soil. In incineration ash generated through incineration of one containing such radioactively contaminated plant or wood, the radioactive cesium may be trapped in glass or the like. The present invention is intended to separate and recover such radioactive cesium compound in a state of being hardly treated.

[0020] The waste contaminated with radioactive cesium is mixed with the CaO source and/or the MgO source after setting the kinds and the blending ratios of the waste and the CaO source and/or the MgO source so that the masses of calcium oxide (CaO), magnesium oxide (MgO), and silicon dioxide (SiO_2) in the mixture to be obtained satisfy the following equation (1):

$$((CaO+1.39\times MgO)/SiO_2)=1.0\ \text{to}\ 2.5 \qquad (1)$$

(where the CaO, the MgO, and the SiO_2 represent a mass of calcium in terms of an oxide, a mass of magnesium in terms of an oxide, and a mass of silicon in terms of an oxide, respectively).

[0021] The lower limit value of the numerical value determined by the equation (1) based on the masses of CaO, MgO, and SiO_2 is preferably 1.2 or more, more preferably 1.4 or more, still more preferably 1.7 or more, even still more preferably 1.8 or more, particularly preferably a value higher than 1. 9, from the viewpoint of increasing the amount of radioactive cesium to be volatilized.

[0022] The upper limit value of the numerical value determined by the equation (1) is preferably 2.4 or less, more preferably 2.3 or less, still more preferably 2.2 or less, even still more preferably 1.9 or less, particularly preferably 1.8 or less, from the viewpoints of volatilizing radioactive cesium in the mixture sufficiently, and concurrently volatilizing potassium and sodium in the mixture in fewer amounts.

[0023] The mass of 1 mole of CaO corresponds to the mass of 1.39 moles of MgO. Therefore, the mass of MgO is multiplied by 1.39 in the equation (1).

[0024] When the mass ratio represented by the equation (1) is less than 1.0, a liquid phase is liable to be generated as a burning temperature becomes higher,resulting in reducing the amount of radioactive cesium to be volatilized. When the mass ratio represented by the equation (1) exceeds 2.5, the total amount of potassium and sodium to be volatilized contained in the mixture of the waste contaminated with radioactive cesium and the CaO source and/or the MgO source is increased, resulting in increasing the amount of a radioactive substance-containing waste as a solid content obtained through cooling of an exhaust gas.

[0025] A chloride such as calcium chloride ($CaCl_2$), potassium chloride (KCl), and sodium chloride (NaCl) may be further used as a material of the mixture described above for the purpose of promoting chloride volatilization of radioactive cesium and reducing the volume of a recovered volatile material. Of those chlorides, calcium chloride is preferred from the viewpoint of promoting chloride volatilization.

[0026] The amount of the chloride is set so that the molar ratio of chlorine to cesium and potassium, that is to say (Cl/(Cs+K)), is preferably 1.00 or less, more preferably from 0.010 to 0.60, still more preferably from 0.015 to 0.40, particularly preferably from 0.03 to 0.30. When the molar ratio is 1.0 or less, potassium and sodium are not volatilized but radioactive cesium is volatilized in a large amount, resulting in reducing the volume of a radioactive substance-containing waste.

[0027] The amount of chlorine in the mixture is preferably 1, 500 mg/kg or less. When the amount of chlorine is 1, 500 mg/kg or less, a liquid phase is hardly generated even at high temperature, and radioactive cesium is volatilized in a large amount.

[0028] It is preferred that the molar ratio (Cl/(Cs+K)) be 1.0 or less and the amount of chlorine in the mixture be 1,500 mg/kg or less. It is more preferred that the molar ratio be 0.5 or less and the amount of chlorine in the mixture be 1,250 mg/kg or less. When such molar ratio and such amount of chlorine are adopted, cesium to be volatilized can be easily volatilized in the form of cesium chloride. In addition, the volume of a recovered material described later can be reduced.

[0029] In the mixing of the waste with the CaO source and/or the MgO source, crushing, grinding, or the like, which doubles as the mixing, may be performed as required. Alternatively, the mixing may be performed in two-stage treatment by combining a crusher or a grinding mill with a mixer. When a rotary kiln described later is used to perform burning, a part of the CaO source, the MgO source, the waste, and the like may be loaded into an inlet end of the kiln as it is, because the materials are rotated and mixed in the rotary kiln. The mixture is preferably formed of grains each having a size less than about 5 mm. Stones or the like each having a size of 5 mm or more and not containing cesium in a large amount may be preliminarily removed by washing with water.

[0030] The heating temperature of the mixture of the waste contaminated with radioactive cesium and the CaO source and/or the MgO source is from 1, 200 to 1, 350°C, preferably from 1, 200 to 1, 300°C.

[0031] When the heating is performed in the above-mentioned temperature range, radioactive cesium contained in the waste can be efficiently volatilized. When the heating temperature is less than 1,200°C, the amount of radioactive cesium to be volatilized is reduced. The case where the heating temperature exceeds 1,350°C is not preferred, because, in such case, radioactive cesium is trapped in a liquid phase to be generated and is hardly volatilized.

[0032] The heating time period of the mixture is preferably 15 minutes or more, and more preferably 30 minutes or more, from the viewpoint of securing a sufficient amount of radioactive cesium to be volatilized. The upper limit of the heating time period is not particularly limited, but is preferably 180 minutes or less, and more preferably 120 minutes or less. When the heating time period exceeds 180 minutes, potassium and sodium are volatilized in large amounts together with radioactive cesium in the mixture.

[0033] In the case where the raw materials are tumbled, such as in a rotary kiln, a high volatilization rate can be achieved in a shorter burning time period as compared to that in the case under the conditions of allowing the raw materials to stand still, by virtue of a high contact rate of gas and radioactive cesium, and a good thermal conductivity.

[0034] As heating means, any one of a continuous type or a batch type may be used.

[0035] As examples of continuous type heating means, a rotary kiln and the like are given.

[0036] As examples of batch type heating means, an incineration furnace, an electric furnace, a microwave heating device, and the like are given.

[0037] Of those heating means, the continuous type heating means is preferably used in the present invention from the viewpoint of enhancing the efficiency of the treatment. A rotary kiln is particularly preferred because a heating temperature and a retention time period of the waste suitable for volatilization of radioactive cesium can be easily provided.

[0038] With regard to the atmosphere during the heating, it is preferred to perform the heating in air containing water vapor, because the amount of an alkali metal (i.e. potassium and sodium) to be volatilized can be reduced, and concurrently the amount of radioactive cesium to be volatilized can be increased.

[0039] In contrast, when the heating is performed in air free of water vapor (i.e. pure air), a larger amount of radioactive cesium can be volatilized, while the amount of an alkali metal (i.e. potassium and sodium) to be volatilized is increased.

[0040] By adjusting the amount of the chloride, the heating temperature, the heating time period, and the amount of water vapor during the heating, the amount of an alkali metal (i.e. potassium and sodium) to be volatilized can be reduced, and concurrently the amount of radioactive cesium to be volatilized can be increased.

[0041] There are cases where the waste contaminated with radioactive cesium contains chromium. In such cases, an obtained burned product may contain hexavalent chromium (Cr^{6+}).

[0042] When such burned product is used as a cement admixture, an aggregate, a civil work material, or the like (particularly as a civil work material), hexavalent chromium contained in the burned product may be eluted to cause water pollution, soil pollution, or the like.

[0043] In view of the foregoing, the heating may be performed in a reducing atmosphere in the heating step. When the heating is performed in a reducing atmosphere, generation of hexavalent chromium susceptible to be generated in an oxidizing atmosphere can be prevented, even when the waste contains chromium. Further, even when the waste is heated temporarily in an oxidizing atmosphere and hexavalent chromium is generated in the step of heating the waste, hexavalent chromium is reduced to trivalent chromium (Cr^{3+}), and the obtained burned product can be safely used as a civil work material or the like. The method of heating in air containing water vapor and the method of heating in a reducing atmosphere may be performed in combination. Methods of performing heating in a reducing atmosphere are hereinafter described, taking as an example the case of using an internal combustion type apparatus (e. g. internal combustion type rotary kiln or the like) of a countercurrent type (i.e. one in which combustion is performed at a raw material outlet side), to which the present invention is not limited.

[0044] As an example of the method of heating the waste contaminated with radioactive cesium in a reducing atmosphere, there is given a method of burning a combustible substance during the heating of the waste. The periphery of the waste can be maintained as a reducing atmosphere through the burning of a combustible substance. Even when the waste contains chromium, generation of hexavalent chromium can be prevented. Further, even when hexavalent chromium is generated in the step of heating the waste, hexavalent chromium is reduced to trivalent chromium.

[0045] Examples of the combustible substance in this case include coal, coke, active carbon, waste wood, waste plastic, heavy oil sludge,and a solid lump of a waste obtained through compression and/or solidification of a waste such as a municipal refuse.

[0046] As a method of supplying the combustible substance, a method of preliminarily mixing the combustible substance with the waste contaminated with radioactive cesium may be adopted. In the case of using a rotary kiln as an apparatus to be used for the heating, a method of supplying the combustible substance to (i.e. through) a waste inlet side, a waste outlet side, or a middle portion of the rotary kiln may be adopted.

[0047] In the case of preliminarily mixing the combustible substance with the raw materials, the mixed amount and grain size of the combustible substance are preferably as large as possible, as long as the combustible substance does not remain in an unburned state in the burned product obtained through the heating.

[0048] Cases of supplying the combustible substance to a waste inlet side of a rotary kiln or to a middle portion of a rotary kiln are described.

[0049] In those cases, the combustible substance is preferably a substance capable of keeping a reducing atmosphere for a long period of time. Specifically, there are given, for example, a combustible substance having a lower combustion velocity as compared to that of a main fuel for the rotary kiln, and a combustible substance having a combustion velocity comparable to that of the main fuel but containing more coarse grains as compared to the main fuel. Specific examples thereof include petroleum coke, coal coke, and anthracite coal. A lower combustion velocity is preferred because the combustible substance can be finer.

[0050] The average grain size of the combustible substance is preferably from 0.5 to 20 mm, and more preferably from 1 to 5 mm. When the average grain size is less than 0.5 mm, the combustible substance is completely burned at the very early stage of the burning, and hence the reducing atmosphere cannot be kept for a long period of time in some cases. When the average grain size exceeds 20 mm, a large amount of the combustible substance remains in an unburned state in the obtained burned product, and hence the supplied combustible substance is wasted in vain. In addition, in the case of using the burned product as a cement admixture or a concrete aggregate, there may arise problems of poor air entraining property of mortar concrete due to adsorption of an AE agent onto remaining unburned carbon, or poor appearance of mortar concrete due to the unburned carbon appearing on the surface of the morter concrete during compaction, and the like.

[0051] The amount of the combustible substance is preferably from 5 to 40 kg, more preferably from 10 to 40 kg, and particularly preferably from 12 to 40 kg with respect to 1,000 kg of the burned product to be obtained through the heating. When the amount is less than 5 kg, an effect obtained by adopting a reducing atmosphere may be reduced. When the amount exceeds 40 kg, a large amount of the combustible substance remains in an unburned state in the obtained burned product. This may lead to poor air entraining property or poor appearance of mortar concrete when the burned product is used as a cement admixture or a concrete aggregate.

[0052] In the case of supplying the combustible substance to a middle portion of a rotary kiln, the combustible substance is preferably supplied to a portion between a position having the highest temperature in the rotary kiln and a waste inlet side.

[0053] In the burning of the combustible substance, the oxygen (O_2) concentration in the furnace is preferably 5 mass% or less, and more preferably 3 mass% or less, from the viewpoint of preventing rapid disappearance of the combustible substance.

[0054] By adjusting the conditions described above, the retention time period, and the like, generation of hexavalent chromium can be prevented and the combustible substance can be prevented from remaining. When the obtained burned product is used as a cement admixture or a concrete aggregate, the conditions described above, the retention time period, and the like are adjusted so that the air entraining property and the appearance of mortar concrete are not adversely affected.

[0055] Next, a case of supplying the combustible substance to a waste outlet side is described.

[0056] The combustible substance may be easily sent by pressure to a waste outlet side (and into the inside) of a furnace by using air. A dedicated inlet port for the combustible substance may be provided at the waste outlet side of a rotary kiln. A coarse combustible substance (e.g. one having an average grain size of about from 1 to 10 mm) may be dropped as a part of a fuel for a main burner.

[0057] The combustible substance is preferably one allowing for a higher reducing condition as compared to those in the cases of supplying the combustible substance to a waste inlet side or to a middle portion of a rotary kiln. Specifically, there is given, for example, a combustible substance having a higher combustion velocity as compared to that of a main fuel for the rotary kiln. Examples of such combustible substance having a high combustion velocity include waste wood, waste plastic, heavy oil sludge, and a solid lump of a waste obtained through compression and/or solidification of a waste such as a municipal refuse.

[0058] The average grain size of the combustible substance is preferably from 0.1 to 10 mm, and more preferably from 1 to 5 mm. When the average grain size is less than 0.1 mm, the combustible substance is completely burned at the very early stage of the burning, and hence the reducing atmosphere cannot be kept in some cases. When the average grain size exceeds 10 mm, a large amount of the combustible substance remains in an unburned state in the obtained burned product, and hence the supplied combustible substance is wasted in vain. This may lead to poor air entraining property or poor appearance of mortar concrete when the burned product is used as a cement admixture or a concrete aggregate. The time period for which a reducing atmosphere can be kept can be adjusted by the average grain size of the combustible substance. For example, a combustible substance having a high combustion velocity can keep a reducing atmosphere for a longer period of time when its average grain size is set larger (i.e. coarser).

[0059] The heat quantity of the combustible substance may be set to generally from 2 to 40% with respect to the heat quantity of the entire fuel to be used for the main burner. When the heat quantity of the combustible substance is less than 2%, an effect obtained by adopting a reducing atmosphere may be reduced. When the heat quantity of the combustible substance exceeds 40%, a large amount of the combustible substance remains in an unburned state in the obtained burned product, and hence the supplied combustible substance is wasted in vain. This may lead to poor air entraining property or poor appearance of mortar concrete when the burned product is used as a cement admixture or a concrete aggregate.

[0060] In the case of supplying the combustible substance to a waste outlet side, only a part of the inside of the furnace is exposed to a reducing atmosphere in the rotary kiln, which is different from the cases of supplying the combustible substance to a waste inlet side or to a middle portion of the rotary kiln. Therefore, it is preferred to set the supply position (i.e. drop position) of the combustible substance to a position nearer to the waste inlet side with respect to a position having the highest temperature in the rotary kiln from the viewpoints of keeping the reducing atmosphere for a long period of time and realizing the reducing atmosphere in a high temperature region offering a high reducing speed. The supply position is preferably set to an inner position (i.e. aposition nearer to the inlet of the kiln) than the position represented as 4D from the outlet of the kiln, given that the inner diameter of the kiln is represented as D. In the case where the position having the highest temperature in the rotary kiln is located at a position closer to the outlet side of the rotary kiln depending on the set conditions of the main burner or the like, the supply position is preferably set to an inner position than the position represented as 3D from the outlet of the kiln. The supply position (i.e. drop position) is preferably adjusted by the angle of the inlet port of the combustible substance, the position of the inlet port, the loading speed of the combustible substance, the grain size of the combustible substance, and the specific density of the combustible substance.

[0061] In the case of adding the combustible substance, the oxygen (O_2) concentration in the furnace (i.e. the rotary kiln) ispreferably 5 mass% or less, and more preferably 3 mass% or less, from the viewpoint of preventing rapid disappearance of the combustible substance.

[0062] It is preferred to prevent the generation of hexavalent chromium and prevent the combustible substance from remaining by adjusting the conditions described above.

[0063] As another method of heating the waste contaminated with radioactive cesium in a reducing atmosphere, there is given a method of putting the waste in direct contact with flame.

[0064] Specifically, the waste contaminated with radioactive cesium and the like are burned in an internal combustion type apparatus (e.g. internal combustion type rotary kiln or the like) while being put in direct contact with flame during its heating (i.e. burning) (hereinafter sometimes referred to as "burning with flame"). As a method of performing burning with flame by using an internal combustion type rotary kiln, the following methods are given: (a) a method of placing a main burner for heating at the bottom of the kiln, to perform heating (i.e. burning) so that the flame licks the waste and the like; (b) a method of adjusting the fuel amount or the air speed to exude the flame, to perform heating (i.e. burning) so that the flame licks the waste and the like; and (c) a method of dropping the angle of the main burner to elongate the flame, to perform heating (i.e. burning) so that the flame licks the waste and the like. In addition to the main burner for heating, an auxiliary burner for burning with flame may be placed. A reduction effect is improved when the contact time period between the waste and the flame is prolonged through adjustment of the conditions. Even when the waste contains chromium, generation of hexavalent chromium can be suppressed. Further, even when hexavalent chromium is generated in the step of heating the waste, hexavalent chromium is reduced to trivalent chromium.

[0065] In the burning with flame, the oxygen concentration is preferably 5 mass% or less, and more preferably 3 mass% or less, from the viewpoint of generating a larger amount of flame.

[0066] An effect of preventing elution of hexavalent chromium can be more improved by adjusting the above-mentioned conditions. The burning of the combustible substance described above and the burning with flame may be used in combination.

[0067] A reducing atmosphere can be achieved through adjustment of the atmosphere during the heating.

[0068] For example, as still another method of heating the waste contaminated with radioactive cesium in a reducing atmosphere, there is given a method of burning a fuel for heating with air in an amount less than the theoretical amount of air.

[0069] Specific examples of such method include: a method of burning the fuel in an internal combustion type apparatus (i.e. internal combustion type rotary kiln or the like) at an air ratio in the furnace (i.e. a ratio of the supplied amount of air to the theoretical amount of air) of from 0.8 to 1.0 or at an oxygen concentration in the furnace of 1 mass% or less; and a method of burning the fuel while keeping the concentration of carbon monoxide in the furnace at from 0.1 to 1.0 mass%.

[0070] When the air ratio is less than 0.8 or the concentration of carbon monoxide exceeds 1.0 mass% in the furnace, it may be difficult to perform burning required for the heating. When the air ratio in the furnace exceeds 1.0, the oxygen concentration in the furnace exceeds 1 mass%, or the fuel is burned while the concentration of carbon monoxide in the furnace is kept at less than 0.1 mass%, a reduction effect is reduced.

[0071] Examples of the fuel for heating include a heavy oil, pulverized coal, a recycled oil, LPG, NPG, and a combustible waste, as a main fuel (i.e. a fuel for a burner). Those fuels are used after being adjusted into a grain size allowing for its burning in a space.

[0072] Such a method using a reducing atmosphere described above may be used in combination with the burning of a combustible substance and/or the burning with flame described above.

[0073] As another example, there is given: a method of replacing the atmosphere in an apparatus to be used for heating (e.g. an external combustion type rotary kiln, an electric furnace, or the like) with an inert gas such as a nitrogen gas; or a method of allowing such gas to flow through the apparatus. In such methods, a mixed gas of an inert gas and a reducing gas such as a carbon monoxide gas maybe used for the replacement or maybe allowed to flow therethrough.

[0074] Volatilized radioactive cesium contained in an exhaust gas generated by the heating method described above can be recovered with a dust collector, a scrubber, or the like after being solidified through cooling. When a preheater is installed before the kiln, the exhaust gas containing volatilized radioactive cesium at a high concentration may be partially extracted to be cooled, to thereby recover radioactive cesium in a solid form. Recovered radioactive cesium can be stored in, for example, a container made of concrete in a sealed state after being subjected to volume reduction treatment such as washing with water or adsorption as required. This enables reduction in volume and storage of the waste containing a radioactive substance without leaking out the waste to the outside.

[0075] When the chloride is added to the mixture of the waste and the CaO source and/or the MgO source, radioactive cesium can be recovered in the form of radioactive cesium chloride. Radioactive cesium chloride can be easily dissolved in water, and thus can also be recovered as an aqueous solution.

[0076] The burned product to be obtained after the heating is ground as required, and can be utilized as a cement admixture, an aggregate (i.e. an aggregate for concrete or an aggregate for asphalt), a civil work material (e.g. a backfill material, a banking material, a base course material, or the like), or the like.

[0077] The burned product to be obtained after the heating has an absolute dry specific density (i.e. a density in absolutely dry condition) of preferably from 1.5 to 3.0 g/cm^3, and more preferably from 2.0 to 3.0 g/cm^3.

[0078] The amount of free lime in the burned product is preferably 1.0 mass% or less, more preferably 0.5 mass% or less, still more preferably 0.2 mass% or less. When the amount of free lime exceeds 1.0 mass%, concrete may be fractured through expansion or the burned product itself may be collapsed in the case of using the burned product as an aggregate for concrete or a civil work material.

[0079] The burned product may be used as a cement admixture or the like after adjustment of its grain size through sieving or the like in consideration of a grain size to be required, compaction property, and the like.

[0080] In the case where the waste contains chromium, elution of hexavalent chromium from the obtained burned product can be prevented by performing treatment described below on the burned product, in addition to the method of heating the waste in a reducing atmosphere in the heating step. Especially in the case of using the burned product as a civil work material, it is preferred to take a measure against elution of hexavalent chromium from the viewpoint of preventing water pollution and soil pollution. A specific method as the measure against elution of hexavalent chromium is hereinafter described.

[0081] As the measure against elution of hexavalent chromium taken in the case where the obtained burned product contains hexavalent chromium, there is given a method of mixing the burned product having high temperature obtained by the heating step with a combustible substance. When the burned product having high temperature after the heating step is mixed with a combustible substance and then cooled, hexavalent chromium contained in the burned product can be reduced to trivalent chromium and its volume can be reduced.

[0082] Specific examples of such method include: a method of mixing the burnedproduct after the heating step with a combustible substance in a blast furnace while keeping the temperature of the burned product at high temperature; and a method involving filling a container with the burned product having high temperature after the heating step and a combustible substance and allowing the mixture of the burned product and the combustible substance to stand still while keeping the temperature of the mixture at high temperature.

[0083] The burned product having high temperature may be mixed with a combustible substance in a cooling step using an air quenching cooler, a rotary cooler, or the like, conducted subsequent to the heating step. Of those, a rotary cooler is preferably used by virtue of less contact with oxygen and a high degree of mixing with a combustible substance.

[0084] In the case where a combustible substance is mixed in in the cooling step, the mixing method for a combustible substance is not particularly limited, but the mixing is preferably performed immediately after the heating step from the viewpoint of keeping high temperature conditions and a reducing atmosphere for a long period of time. For example, in the case of performing heating in a rotary kiln, a method involving dropping a combustible substance at an outlet end of the rotary kiln and mixing the combustible substance with the burned product is preferred.

[0085] In the case where a combustible substance is mixed with the burned product, the temperature of the burned product is preferably 800°C or more, and more preferably 1,000°C or more, because a higher temperature exhibits a greater effect of reducing the volume of hexavalent chromium. In the case of performing heating by using a rotary kiln, the temperature of the burned product during the mixing in a rotary cooler can be increased by setting a position having the highest burning temperature in the rotary kiln closer to an outlet end side.

[0086] When the time period until the burned product is cooled after mixing with a combustible substance is longer, an effect of reducing the volume of hexavalent chromium is more improved. The time period until the temperature of the burned product reaches 600°C or less after the mixing is preferably 1 minute or more, and more preferably 3 minutes or more.

[0087] The combustible substance is mixed in an amount corresponding to heat quantity of preferably from 2 to 20% with respect to the heat quantity of the entire mixture containing the burned product and the combustible substance. When the amount corresponds to heat quantity of less than 2%, an effect of reducing the volume of hexavalent chromium is reduced. When the amount corresponds to heat quantity exceeding 20%, a large amount of the combustible substance remains in an unburned state in the burned product after the cooling.

[0088] Examples of the combustible substance include coal, coke, active carbon, waste wood, waste plastic, heavy oil sludge, and a solid lump of a waste obtained through compression and/or solidification of a waste such as a municipal refuse. Of those combustible substances, one allowing for a high reducing condition is preferred. Specifically, there is given a combustible substance having a high combustion velocity. Examples of such combustible substance having a high combustion velocity include waste wood, waste plastic, heavy oil sludge, and a solid lump of a waste obtained through compression and/or solidification of a waste such as a municipal refuse.

[0089] The average grain size of the combustible substance is preferably from 0.1 to 10 mm, and more preferably from 1 to 5 mm. When the average grain size exceeds 10 mm, a large amount of the combustible substance remains in the burned product after the cooling. When the average grain size is less than 0.1 mm, an effect of reducing the volume of hexavalent chromium is reduced, and the amount of the combustible substance to be mixed with the burned product is reduced owing to scattering of the supplied combustible substance caused by a wind speed of cooling air or the like.

[0090] The combustible substance having a high combustion velocity described above can be set to have a larger average grain size (i.e. be coarser). When the average grain size is set larger, it is possible to prolong the time period for which a reducing atmosphere can be kept and prevent scattering of the supplied combustible substance caused by a wind speed of cooling air or the like.

[0091] The oxygen concentration in the mixing with the combustible substance is not particularly limited. If possible, an exhaust gas may be utilized from the viewpoint of achieving less contact with oxygen or reducing the amount of the combustible substance to be added.

[0092] The conditions described above are preferably adjusted so that an effect of reducing the volume of hexavalent chromium is improved and the combustible substance is prevented from remaining. In the case of using the burned product as a cement admixture, the conditions are preferably adjusted so that cement using the burned product is prevented from discoloring, such discoloring being caused by adopting an excessively high reducing atmosphere.

[0093] As another measure against elution of hexavalent chromium, there is given a method of further heating the burned product obtained by the heating step to melt the burned product.

[0094] Hexavalent chromium contained in the burned product is confined in glass through melting of the burned product.

Thus, in the case of using the burned product as a civil work material or the like, the amount of hexavalent chromium to be eluted is reduced to its environmental limit value or less.

[0095] After the burned product is further heated to be melted, the resultant molten material is cooled to be in a granular form. The obtained granular molten material can be used as an aggregate for concrete by virtue of a low water absorption rate and high strength. The molten material may be cooled by rapid cooling or gradual cooling.

[0096] It is preferred to directly melt the burned product having high temperature obtained by the heating step (for example, the burned product immediately after coming out from a kiln) from the viewpoint of energy cost.

[0097] As still another measure against elution of hexavalent chromium, there may be performed a mixing step of mixing the burned product obtained by the heating step with at least one kind or more selected from the group consisting of a reducing agent and an adsorbent.

[0098] For example, when the burned product is mixed with a reducing agent, hexavalent chromium contained in the burned product or eluted from the burned product can be reduced to trivalent chromium.

[0099] Examples of such reducing agent include sulfites such as sodium sulfite, salts of iron(II) such as iron(II) sulfate and iron(II) chloride, sodium thiosulfate, and iron powder.

[0100] When the burned product is mixed with an adsorbent, hexavalent chromium eluted from the burned product is adsorbed thereon. Thus, hexavalent chromium can be insolubilized or prevented from being eluted.

[0101] Examples of such adsorbent include: one kind or a mixture of two or more kinds selected from: a layered double hydroxide such as zeolite, a clay mineral, and a hydrotalcite compound such as a Mg-Al based hydrotalcite compound and a Mg-Fe based hydrotalcite compound; a Ca-Al based compound such as a Ca-Al based hydroxide, ettringite, and a monosulfate; a hydrous oxide such as iron oxide (hematite) and bismuth oxide; a magnesium compound such as magnesium hydroxide, light burned magnesium, burned dolomite, and magnesium oxide; an iron compound such as iron sulfide, iron powder, schwertmannite, and FeOOH; silicon oxide, aluminum oxide, iron oxide, and a mixture or a burned product using one or more thereof; a compound containing cerium; and a compound containing another rare earth element.

[0102] Those reducing agents and adsorbents may be used alone or two or more kinds thereof may be used in combination.

[0103] As a method of mixing the burned product with an agent (i.e. reducing agent and/or adsorbent), there are given the following methods: a method of mixing the burned product with the agent in a powder form; a method involving preliminarily mixing the agent and water to provide a slurry or an aqueous solution (hereinafter sometimes referred to as "slurry or the like") and then mixing the burned product with the slurry or the like; a method of spraying the slurry or the like to the burned product; and a method of immersing the burned product in the slurry or the like.

[0104] The amount of the agent to be used is adjusted so that the amount of a metal salt per 100 kg of the burned product is preferably from 0.01 to 10 kg, more preferably from 0.1 to 7 kg, and particularly preferably from 0.2 to 5 kg. The amount of the agent is adjusted by the amount of the agent in a powder form, the concentration of the slurry or the like, the spray amount of the slurry or the like, and the amount of the burned product to be put into the slurry or the like. When the amount of a metal salt per 100 kg of the burned product is less than 0.01 kg, an effect of reducing the amount of hexavalent chromium to be eluted is reduced. The case where the amount exceeds 10 kg is not economical owing to saturation of the effect of reducing the amount of hexavalent chromium to be eluted.

[0105] The temperature of the burned product in the mixing is preferably from 100 to 800°C, more preferably from 125 to 600°C, and particularly preferably from 150 to 400°C. The case where the temperature of the burned product exceeds 800°C is not preferred because, in such case, cracks occur in the burned product or the burned product becomes finer, resulting in a reduction in strength. The case where the temperature of the burned product is less than 100°C is not preferred because, in such case, the agent is hardly attached onto the surface of the burned product.

[0106] The method of spraying the slurry or the like containing the agent to the burned product having high temperature is preferred because the agent is attached onto the surface of the burned product and is hardly peeled off therefrom. In the case where the burned product includes pores, the method of immersing the burned product in the slurry or the like is preferred because the agent penetrates well into the inside of the burned product and is attached onto the surface of the burned product as well.

[0107] As yet still another measure against elution of hexavalent chromium, there is given a method of washing with water the burned product obtained by the heating step.

[0108] Examples of such water washing method include: (i) a washing method of spraying a wash solution with a sprinkler or the like onto the burned product in a container or on a conveyer belt; (ii) a washing method involving repeating: putting the burned product and a washing solution in a container and immersing the burned product in the washing solution for a certain period of time; discharging the washing solution after the immersion; and supplying a new washing solution; and (iii) a washing method of replacing the burned product in order while immersing the burned product in a washing solution by using a trommel or the like.

[0109] As the washing solution, even tap water may be generally used. Alternatively, an aqueous solution containing the above-mentioned agent (i.e. reducing agent or adsorbent) may be used. The washing solution after the washing may be reused as the washing solution or disposed after treatment.

[0110] The time period of water washing, the number of times of water washing, and the amount of the washing solution to be used for water washing are not particularly limited. The water washing may be performed until the amount of hexavalent chromium to be eluted reaches its environmental limit value (Notification No. 46 from the Environment Agency).

[0111] Those methods may be performed in combination with the method of heating the waste in a reducing atmosphere in the heating step described above.

[0112] The burned product to be obtained by the heating step of the present invention has an excellent ability to fix a heavy metal (e.g. lead, arsenic, and the like) other than hexavalent chromium therein, and hence can be suitably used as a civil work material (e. g. a backfill material, a banking material, a base course material, or the like) after the treatment for preventing elution of hexavalent chromium described above.

[0113] The burned product obtained by the heating step can be used as a cement admixture after grinding. The burned product after grinding may be mixed with 1 to 6 parts by mass of gypsum in terms of SO_3 with respect to 100 parts by mass of the burned product.

[0114] The grinding method is not particularly limited. For example, grinding may be performed by an ordinary method using a ball mill or the like.

[0115] The burned product after grinding preferably has a Blaine specific surface area of from 2,500 to 5, 000 cm^2/g from the viewpoints of a reduction in bleeding of mortar or concrete, flowability, and strength expressing property.

[0116] The burned product, cement clinker, and gypsum may be concurrently ground. Cement obtained through the concurrent grinding preferably has a Blaine specific surface of from 2,500 to 4,500 cm^2/g from the viewpoints of a reduction in bleeding of mortar or concrete, flowability, and strength expressing property.

[0117] When the cement admixture is mixed with cement to provide a cement composition, the cement composition can exhibit low hydration heat and good flowability.

[0118] The burned product obtained by the heating step can be used as an aggregate (i.e. an aggregate for concrete or an aggregate for asphalt) or a civil work material after grinding or classification as required.

[0119] When the burned product containing hexavalent chromium is used as an aggregate, hexavalent chromium is trapped in a cement hardened material. Therefore, the elution of hexavalent chromium can be prevented by protecting the aggregate from rain during its transportation or storage. The treatment for preventing elution of hexavalent chromium described above may be performed.

[0120] The obtained burned product can be utilized as both of a fine aggregate and a coarse aggregate. When used as a coarse aggregate, the burned product is used after being adjusted into a grain size of 5 mm or more through sieving or the like.

[0121] When the obtained burned product is used as a civil workmaterial, the burned product is used after being adjusted into a grain size of from 0.1 to 100 mm in view of compaction property and the like.

[0122] In the case where the burned product is used as an aggregate, the absolute dry specific density of the burned product is preferably from 2.0 to 3.0 g/cm^3. When the absolute dry specific density is less than 2.0 g/cm^3, the strength of concrete may be reduced. The water absorption rate of the burned product is preferably 15% or less. When the water absorption rate exceeds 15%, the strength of concrete may be reduced.

[0123] Particularly in the case where the burned product is used as an aggregate for concrete, it is preferred that the burned product have an absolute dry specific density of from 2.5 to 3.0 g/cm^3 and a water absorption rate of 3% or less.

[0124] The amount of free lime is preferably 1.0 mass% or less, and more preferably 0.5 mass% or less. When the amount of free lime exceeds 1.0 mass%, concrete may be fractured through expansion.

Examples

[0125] Now, the present invention is described in more detail by way of Examples. However, the present invention is not limited to Examples.

[Synthesis Example 1; Production of clay A having cesium adsorbed thereon]

[0126] 500 g of bentonite were immersed in 2 liters of an aqueous solution containing cesium at a concentration of 250 mg/liter for 1 day. After that, a solid content was recovered through centrifugal separation, followed by washing with water and then centrifugal separation again. Thus, clay A having cesium adsorbed thereon containing cesium at a concentration of 1,060 mg/kg was obtained.

[Synthesis Example 2; Production of clay B having cesium adsorbed thereon]

[0127] 500 g of bentonite were immersed in 2 liters of an aqueous solution containing cesium at a concentration of 500 mg/liter for 1 day. After that, a solid content was recovered through centrifugal separation, followed by washing with water and then centrifugal separation again. Thus, clay B having cesium adsorbed thereon containing cesium at a concentration of 2,200 mg/kg was obtained.

[Example 1]

[0128] 6.6 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1 and 13.2 g of limestone powder were mixed with each other. The obtained mixture was heated at 1,300°C for 60 minutes in air free of water vapor (i.e. pure air) by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs) and chlorine (Cl) through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 1.

[Example 2]

[0129] 6.6 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1 and 13.2 g of limestone powder were mixed with each other. The obtained mixture was heated at 1,300°C for 60 minutes in air (water content: 7%), which has be obtained by being bubbled through water at 60°C, by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 1.

[0130] The heating in air having a water content of 7% was performed for the purpose of simulating heating in an actual internal combustion type kiln.

[Example 3]

[0131] 8 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1 and 12 g of limestone powder were mixed with each other. The obtained mixture was heated at 1,300°C for 60 minutes in air (water content: 7%), which has be obtained by being bubbled through water at 60°C, by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 1.

[Example 4]

[0132] 9 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1 and 11 g of limestone powder were mixed with each other. The obtained mixture was heated at 1,300°C for 60 minutes in air (water content: 7%), which has be obtained by being bubbled through water at 60°C, by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 1.

[Example 5]

[0133] 10 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1 and 10 g of limestone powder were mixed with each other. The obtained mixture was heated at 1,300°C for 60 minutes in air (water content: 7%), which has be obtained by being bubbled through water at 60°C, by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 1.

[Example 6]

[0134] 6.6 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1 and 13.2 g of limestone powder were mixed with each other. The obtained mixture was heated at 1,200°C for 60 minutes in pure air by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 1.

[Example 7]

[0135] 11 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1 and 9 g of limestone powder were mixed with each other. The obtained mixture was heated at 1,200°C for 60 minutes in air (water content: 7%), which has be obtained by being bubbled through water at 60°C, by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 1.

[Comparative Example 1]

[0136] The clay A having cesium adsorbed thereon obtained in Synthesis Example 1 was heated at 1,000°C for 60 minutes in pure air by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 1. When the clay having cesium adsorbed thereon was burned at 1,200°C, the sample was melted to cling to a container, and hence was not able to be recovered.

[Comparative Example 2]

[0137] 6.6 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1 and 13.2 g of limestone powder were mixed with each other. The obtained mixture was heated at 1,000°C for 60 minutes in pure air by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 1.

[Table 1]

	Heating temperature	Heating time period	Heating atmosphere	Mass ratio of (CaO+1.39MgO)/SiO_2	Molar ratio of (Cl/(Cs+K))	Content (on ignition basis)				Volatilization rate		
						Cs	Cl	K_2O	Na_2O	Cs	K	Na
						(mg/kg)		(mass%)		(mass%)		
Example 1	Before heating	-	Pure air	1.8	0.016	506	73	0.58	1.74	-	-	-
	1,300°C	60 minutes				30		0.21	1.57	94	64	10
Example 2	Before heating	-	Air (water content: 7%)	1.8	0.016	506	73	0.58	1.74	-	-	-
	1,300°C	60 minutes				46		0.35	1.65	91	40	5
Example 3	Before heating	-	Air (water content: 7%)	1.4	0.016	585	84	0.67	2.01	-	-	-
	1,300°C	60 minutes				53		0.49	1.97	91	27	2
Example 4	Before heating	-	Air (water content: 7%)	1.2	0.016	641	92	0.73	2.20	-	-	-
	1,300°C	60 minutes				160		0.61	2.16	75	17	2
Example 5	Before heating	-	Air (water content: 7%)	1.1	0.016	694	100	0.79	2.38	-	-	-
	1,300°C	60 minutes				340		0.68	2.36	51	14	1
Example 6	Before heating	-	Pure air	1.8	0.016	506	73	0.58	1.74	-	-	-
	1,200°C	60 minutes				354		0.52	1.72	30	10	1
Example 7	Before heating	-	Air (water content: 7%)	1.0	0.016	745	107	0.85	2.55	-	-	-
	1,200°C	60 minutes				589		0.83	2.52	21	2	1
Comparative Example 1	Before heating	-	Pure air	0.1	0.016	1,110	160	1.26	3.80	-	-	-
	1,000°C	60 minutes				1,088		1.23	3.80	2	2	0
	1,200°C	60 minutes				Not recovered				-	-	-

(continued)

	Heating temperature	Heating time period	Heating atmosphere	Mass ratio of (CaO+1.39MgO)/SiO_2	Molar ratio of (Cl/(Cs+K))	Content (on ignition basis)				Volatilization rate		
						Cs	Cl	K_2O	Na_2O	Cs	K	Na
						(mg/kg)		(mass%)		(mass%)		
Comparative Example 2	Before heating	-	Pure air	1.8	0.016	506	73	0.58	1.57	-	-	-
	1,000°C	60 minutes				496		0.57	1.55	2	2	1

[0138] The results of Examples 1 to 7 in Table 1 reveal that cesium can be volatilized by setting the numerical value determined by the equation $((CaO+1.39\times MgO)/SiO_2)$ based on the masses of calcium oxide (CaO), magnesium oxide (MgO), and silicon oxide (SiO_2) in the mixture to about from 1.0 to 1.8 and performing heating at about from 1,200 to 1,300°C.

[0139] Comparison between Example 1 and Examples 2 to 5 (particularly, between Example 1 and Example 2) reveals that heating in air containing water vapor can provide lower volatilization rates of potassium and sodium, and a high volatilization rate of cesium.

[Example 8]

[0140] 30 g of the clay B having cesium adsorbed thereon obtained in Synthesis Example 2, 60 g of limestone powder, and 0.0246 g of calcium chloride were ground and mixed with each other. 20 g of the obtained mixture were heated at 1,300°C for 60 minutes in air (water content: 7%), which has be obtained by being bubbled through water at 60°C, by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 2.

[Example 9]

[0141] 30 g of the clay B having cesium adsorbed thereon obtained in Synthesis Example 2, 60 g of limestone powder, and 0.0492 g of calcium chloride were ground and mixed with each other. 20 g of the obtained mixture were heated at 1,300°C for 60 minutes in air (water content: 7%), which has be obtained by being bubbled through water at 60°C, by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 2.

[Example 10]

[0142] 30 g of the clay B having cesium adsorbed thereon obtained in Synthesis Example 2, 60 g of limestone powder, and 0.0492 g of calcium chloride were ground and mixed with each other. 20 g of the obtained mixture were heated at 1,300°C for 120 minutes in air (water content: 7%), which has be obtained by being bubbled through water at 60°C, by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 2.

[Example 11]

[0143] 30 g of the clay B having cesium adsorbed thereon obtained in Synthesis Example 2, 60 g of limestone powder, and 0.0984 g of calcium chloride were ground and mixed with each other. 20 g of the obtained mixture were heated at 1,300°C for 60 minutes in air (water content: 7%), which has be obtained by being bubbled through water at 60°C, by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 2.

[Example 12]

[0144] 30 g of the clay B having cesium adsorbed thereon obtained in Synthesis Example 2, 60 g of limestone powder, and 0.246 g of calcium chloride were mixed with each other. 20 g of the obtained mixture were heated at 1,300°C for 60 minutes in air (water content: 7%), which has be obtained by being bubbled through water at 60°C, by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 2.

[Example 13]

[0145] 10 g of the clay B having cesium adsorbed thereon obtained in Synthesis Example 2, 10 g of limestone powder, and 0.49 g of calcium chloride were mixed with each other. The obtained mixture was heated at 1,200°C for 60 minutes in pure air by using a tubular electricfurnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of Cs and Cl through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 2.

[Table 2]

	Heating temperature	Heating time period	Heating atmosphere	Mass ratio of (CaO+1.39MgO)/SiO_2	Molar ratio of (Cl/(Cs+K))	Content (on ignition basis)				Volatilization rate		
						Cs	Cl	K_2O	Na_2O	Cs	K	Na
						(mg/kg)		(mass%)		(mass%)		
Example 8	Before heating	-	Air (water content: 7%)	1.8	0.087	1,020	410	0.58	0.85	-	-	-
	1,300°C	60 minutes				51		0.28	0.84	95	53	1
Example 9	Before heating	-	Air (water content: 7%)	1.8	0.138	1,020	640	0.58	0.85	-	-	-
	1,300°C	60 minutes				102		0.31	0.77	90	46	10
Example 10	Before heating	-	Air (water content: 7%)	1.8	0.138	1,020	640	0.58	0.85	-	-	-
	1,300°C	120 minutes				31		0.12	0.42	97	80	51
Example 11	Before heating	-	Air (water content: 7%)	1.8	0.261	1,020	1,210	0.58	0.85	-	-	-
	1,300°C	60 minutes				102		0.41	0.83	90	30	2
Example 12	Before heating	-	Air (water content: 7%)	1.9	0.604	1,020	2,800	0.58	0.85	-	-	-
	1,300°C	60 minutes				408		0.17	0.38	60	70	55
Example 13	Before heating	-	Pure air	1.1	3.219	1,450	20,630	0.80	1.18	-	-	-
	1,200°C	60 minutes				667		0.47	0.54	54	41	54

[0146] The results of Examples 8 to 13 in Table 2 reveal that cesium is volatilized even when a chloride is added. Particularly from the results of Examples 8, 9, and 11, it is revealed that the volatilization rate of cesium is improved while the volatilization rates of sodium and potassium are kept low in the cases where the molar ratio of chlorine to cesium and potassium, (Cl/(Cs+K)), is about from 0.09 to 0.26, the amount of chlorine is about from 410 to 1,210 mg/kg, and the heating time period is about 60 minutes.

[Example 14]

[0147] A burned product was obtained in the same manner as in Example 1 except that the heating was performed at 1,300°C for 120 minutes in air free of water vapor (i. e. pure air). The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs), chlorine (Cl), Na_2O, and K_2O in the same manner as in Example 1, and the volatilization rates of Cs, Na, and K (mass%) were determined. The results are shown in Table 3.

[Example 15]

[0148] A burned product was obtained in the same manner as in Example 1 except that the heating was performed at 1,300°C for 30 minutes in air free of water vapor (i. e. pure air). The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs), chlorine (Cl), Na_2O, and K_2O in the same manner as in Example 1, and the volatilization rates of Cs, Na, and K (mass%) were determined. The results are shown in Table 3.

[Example 16]

[0149] A burned product was obtained in the same manner as in Example 1 except that the heating was performed at 1,250°C for 60 minutes in air free of water vapor (i.e. pure air). The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs), chlorine (Cl), Na_2O, and K_2O in the same manner as in Example 1, and the volatilization rates of Cs, Na, and K (mass%) were determined. The results are shown in Table 3.

[Example 17]

[0150] A burned product was obtained in the same manner as in Example 1 except that the heating was performed at 1,250°C for 120 minutes in air free of water vapor (i.e. pure air). The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs), chlorine (Cl), Na_2O, and K_2O in the same manner as in Example 1, and the volatilization rates of Cs, Na, and K (mass%) were determined. The results are shown in Table 3.

[Example 18]

[0151] A burned product was obtained in the same manner as in Example 1 except that the heating was performed at 1,350°C for 30 minutes in air free of water vapor (i.e. pure air). The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs), chlorine (Cl), Na_2O, and K_2O in the same manner as in Example 1, and the volatilization rates of Cs, Na, and K (mass%) were determined. The results are shown in Table 3.

[Table 3]

	Heating temperature	Heating time period	Heating atmosphere	Mass ratio of (CaO+1.39MgO)/SiO_2	Molar ratio of (Cl/(Cs+K))	Content (on ignition basis)				Volatilization rate		
						Cs	Cl	K_2O	Na_2O	Cs	K	Na
						(mg/kg)		(mass%)		(mass%)		
Example 14	Before heating	-	Pure air	1.8	0.016	506	73	0.58	1.74	-	-	-
	1,300°C	120 minutes				15	-	0.28	1.35	97	52	22
Example 15	Before heating	-	Pure air	1.8	0.016	506	73	0.58	1.74	-	-	-
	1,300°C	30 minutes				119	-	0.57	1.73	76	1	1
Example 16	Before heating	-	Pure air	1.8	0.016	506	73	0.58	1.74	-	-	-
	1,250°C	60 minutes				60	-	0.45	1.70	88	22	2
Example 17	Before heating	-	Pure air	1.8	0.016	506	73	0.58	1.74	-	-	-
	1,250°C	120 minutes				2	-	0.32	1.68	100	44	3
Example 18	Before heating	-	Pure air	1.8	0.016	506	73	0.58	1.74	-	-	-
	1,350°C	30 minutes				30	-	0.55	1.43	94	5	18

[Example 19]

[0152] 30 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1 and 68 g of limestone powder were mixed with each other. The obtained mixture was heated at 1,300°C for 60 minutes in air free of water vapor (i.e. pure air) by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs) and chlorine (Cl) through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 4.

[Example 20]

[0153] 30 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1 and 77 g of limestone powder were mixed with each other. The obtained mixture was heated at 1,300°C for 60 minutes in air free of water vapor (i.e. pure air) by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs) and chlorine (Cl) through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 4.

[Example 21]

[0154] 30 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1, 77 g of limestone powder, and 0.122 g of calcium chloride were mixed with each other. The obtained mixture was heated at 1,300°C for 60 minutes in air free of water vapor (i.e. pure air) by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs) and chlorine (Cl) through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 4.

[Example 22]

[0155] 30 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1, 77 g of limestone powder, and 0.122 g of calcium chloride were mixed with each other. The obtained mixture was heated at 1,250°C for 60 minutes in air free of water vapor (i.e. pure air) by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs) and chlorine (Cl) through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 4.

[Example 23]

[0156] 30 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1 and 90 g of limestone powder were mixed with each other. The obtained mixture was heated at 1,300 °C for 60 minutes in air free of water vapor (i.e. pure air) by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs) and chlorine (Cl) through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 4.

[Example 24]

[0157] 30 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1 and 90 g of limestone powder were mixed with each other. The obtained mixture was heated at 1,250 °C for 60 minutes in air free of water vapor (i.e. pure air) by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs) and chlorine (Cl) through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined.

The results are shown in Table 4.

[Example 25]

[0158] 30 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1, 90 g of limestone powder, and 0.039 g of calcium chloride were mixed with each other. The obtained mixture was heated at 1,300°C for 60 minutes in air free of water vapor (i.e. pure air) by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs) and chlorine (Cl) through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 4.

[Example 26]

[0159] 30 g of the clay A having cesium adsorbed thereon obtained in Synthesis Example 1, 90 g of limestone powder, and 0.039 g of calcium chloride were mixed with each other. The obtained mixture was heated at 1,250°C for 60 minutes in air free of water vapor (i.e. pure air) by using a tubular electric furnace. Thus, a burned product was obtained. The mixture before heating and the burned product obtained through heating were each measured for the contents of cesium (Cs) and chlorine (Cl) through a wet method and the volatilization rate of Cs (mass%) was determined. The amounts of Na_2O and K_2O were each measured by X-ray fluorescence analysis (XRF), and the volatilization rates of Na and K (mass%) were determined. The results are shown in Table 4.

[Table 4]

	Heating temperature	Heating time period	Heating atmosphe re	Mass ratio of (CaO+1.39MgO)/SiO_2	Molar ratio of (Cl/(Cs+K))	Content (on ignition basis)				Volatilization rate		
						Cs	Cl	K_2O	Na_2O	Cs	K	Na
						(mg/kg)		(mass%)		(mass%)		
Example 19	Before heating	-	Pure air	2.0	0.016	447	64	0.51	1.53	-	-	-
	1,300°C	60 minutes				27	-	0.18	1.30	94	65	15
Example 20	Before heating	-	Pure air	2.2	0.016	396	57	0.46	1.36	-	-	-
	1,300°C	60 minutes				20	-	0.13	1.17	95	71	14
Example 21	Before heating	-	Pure air	2.2	0.32	396	1,140	0.46	1.36	-	-	-
	1,300°C	60 minutes				8	-	0.11	0.68	98	75	50
Example 22	Before heating	-	Pure air	2.2	0.32	396	1,140	0.46	1.36	-	-	-
	1,250°C	60 minutes				59	-	0.23	1.23	85	50	10
Example 23	Before heating	-	Pure air	2.5	0.016	319	46	0.37	1.11	-	-	-
	1,300°C	60 minutes				6	-	0.10	0.89	98	73	20
Example 24	Before heating	-	Pure air	2.5	0.016	319	46	0.37	1.11	-	-	-
	1,250°C	60 minutes				29	-	0.21	1.02	91	45	8
Example 25	Before heating	-	Pure air	2.5	0.16	319	460	0.37	1.11	-	-	-
	1,300°C	60 minutes				3	-	0.06	0.50	99	85	55
Example 26	Before heating	-	Pure air	2.5	0.16	319	460	0.37	1.11	-	-	-
	1,250°C	60 minutes				16	-	0.15	0.98	95	60	12

Claims

1. A method of removing radioactive cesium, comprising a heating step of heating a waste contaminated with radioactive cesium and a CaO source and/or a MgO source at a temperature of from 1,200 to 1,350°C to volatilize the radioactive cesium in the waste,
wherein in the heating step, kinds and blending ratios of the waste, the CaO source, and the MgO source are set so that masses of CaO, MgO, and SiO_2 satisfy the following equation (1):

$$((CaO+1.39\times MgO)/SiO_2)=1.0 \text{ to } 2.5 \qquad (1)$$

(in the equation (1), the CaO, the MgO, and the SiO_2 inrepresent a mass of calcium in terms of an oxide, a mass of magnesium in terms of an oxide, and a mass of silicon in terms of an oxide, respectively).

2. A method of removing radioactive cesium according to claim 1, wherein the heating step further comprises using a chloride.

3. A method of removing radioactive cesium according to claim 1 or 2, wherein the heating in the heating step is performed in a reducing atmosphere.

4. A method of producing a burned product, comprising a heating step of heating a waste contaminated with radioactive cesium and a CaO source and/or a MgO source at a temperature of from 1,200 to 1,350°C to volatilize the radioactive cesium in the waste and then produce a burned product,
wherein in the heating step, kinds and blending ratios of the waste, the CaO source, and the MgO source are set so that masses of CaO, MgO, and SiO_2 satisfy the following equation (1):

$$((CaO+1.39\times MgO)/SiO_2)=1.0 \text{ to } 2.5 \qquad (1)$$

(in the equation (1), the CaO, the MgO, and the SiO_2 represent a mass of calcium in terms of an oxide, a mass of magnesium in terms of an oxide, and a mass of silicon in terms of an oxide, respectively).

5. A method of producing a burned product according to claim 4, wherein the heating in the heating step is performed in a reducing atmosphere.

6. A method of producing a burned product according to claim 4 or 5, further comprising a mixing step of mixing the burned product obtained by the heating step with at least one kind selected from the group consisting of a reducing agent and an adsorbent.

7. A cement admixture which is obtained by grinding a burned product obtained by the method of producing a burned product according to any one of claims 4 to 6.

8. An aggregate which is made of a burned product obtained by the method of producing a burned product according to any one of claims 4 to 6.

9. A civil work material which is made of a burned product obtained by the method of producing a burned product according to any one of claims 4 to 6.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
G21F9/32(2006.01)i, *G21F9/28*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G21F9/32, G21F9/28

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Kokai Jitsuyo Shinan Koho	1971-2013	Toroku Jitsuyo Shinan Koho	1994-2013

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2004-37458 A (Technip France), 05 February 2004 (05.02.2004), entire text; all drawings & US 2004/0024277 A1 & EP 1383137 A1 & DE 60323016 D & FR 2841370 A & FR 2841370 A1 & RU 2318259 C & AT 405934 T	1-9
A	JP 2003-315499 A (Mitsubishi Heavy Industries, Ltd.), 06 November 2003 (06.11.2003), entire text; all drawings (Family: none)	1-9

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search 28 January, 2013 (28.01.13)	Date of mailing of the international search report 05 February, 2013 (05.02.13)
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REFERENCES CITED IN THE DESCRIPTION

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- JP 5157897 A **[0005]**