

SPECIFICATION

Sulfur Materials and Method for Producing the Same

[Technical Field]

The present invention relates to a technique for recycling wastes, which is capable of producing sulfur materials useful for civil engineering or construction materials, by treating materials containing a large quantity of chlorides such as sodium chloride unsuitable for concrete materials, with sulfur.

[Background Art]

When inorganic materials, typically incinerated ash containing a large quantity of chlorides such as sodium chloride are used for aggregates for concretes, it is presumable that the working life of the resulting concrete structures or civil engineering buildings is expected to be extremely shortened due to the elution of chlorides which could corrode reinforcing steels and thus causes the concrete to crack or peel off.

Therefore, aggregates for concretes have been used, selectively from those containing chlorides in an amount less than a stipulated amount or have needed a pretreatment with a fresh water for a long time if

containing a large amount of chlorides.

However, such works are considerably large burdens in view of time and cost. Moreover, due to the necessity of use of the specific materials, the construction site where the materials are used is not always close to the site where the materials are procured, also resulting in a large burden associated with time and cost for transportation of the materials. As a result, there arise problems that a place for temporarily storing the materials must be reserved and an extra stock thereof must be always retained so as to be supplied at the timing necessary for construction.

Furthermore, the use of materials such as incinerated ash, containing toxic heavy metals was not also practical from the aspects of facilities and cost because the materials must undergo a water-washing treatment, after which volumes of toxic waste water are produced and thus indispensably need post-treatment facilities such as a waste water treatment facility.

A technique has been demanded which can utilize not only materials such as sea sand and incinerated ash which contain chlorides such as sodium chloride in an amount more than a stipulated amount and thus require a pretreatment including a fresh-water treatment

before being used as aggregates but also those such as incinerated ash, fly ash, and steel slag the use of which for concrete involves difficulties due to the inclusion of toxic substances like general non-industrial and industrial wastes.

The object of the present invention is to provide a sulfur material useful as aggregates for a concrete for civil engineering and construction and as those for a mortar and a method for producing such a sulfur material by treating with sulfur or a modified sulfur a material such as sea sand or incinerated ash, which needs a pretreatment such as fresh-water washing to be used as the aggregates because the material contains chlorides such as sodium chloride in an amount more than a stipulated amount, or a material such as incinerated ash, fly ash, or steel slag, the use of which for concrete involves difficulties because the material contains toxic substances like general non-industrial or industrial wastes.

[Disclosure of the Invention]

The present invention relates to a method for producing a sulfur material wherein it is produced by melting and mixing (A) a sulfur binder in an amount of

10 to 50 percent by mass and (B) an inorganic material of a chloride concentration of 0.02 to 10 percent by mass in an amount of 50 to 90 percent by mass, at a temperature of 119 to 155°C and granulating the melted mixture.

The term "chloride concentration" used herein denotes a value measured by "Test of Chloride Content in Fine Aggregates (Mohr's method)" defined by the Japan Society of Civil Engineering.

The present invention will be described in more detail below.

Component (A), i.e., a sulfur binder is contained in an amount of 10 to 50 percent by mass, based on the total mass of Components (A) and (B). Component (A) of less than 10 percent by mass fails to wet and cover the inorganic material sufficiently and thus could not suppress elution of chlorides sufficiently while Component (A) of more than 50 percent by mass fails to provide the resulting sulfur material with such a sufficient strength to be used as aggregates for a concrete and a mortar.

Examples of (A) sulfur binders used in the present invention include sulfur, modified sulfurs obtained by

modifying sulfur by the reaction of sulfur with another compound, and mixtures thereof.

Sulfur may be normal monomeric sulfurs which may be natural ones or products resulting from desulfurization of a petroleum or a natural gas.

The modified sulfurs may be those modified with a sulfur modifier, such as those obtained by adding to sulfur a sulfur modifier which may be olefinic hydrocarbons; diolefinic hydrocarbons; cycloolefinic hydrocarbons such as dicyclopentadiene and oligomers thereof, cyclopentadiene, tetrahydroindene (THI), and limonene; and aromatic hydrocarbons such as styrene, vinyl toluene, and methyl styrene, each having 4 to 20 carbon atoms and heating the mixture at a predetermined temperature. Sulfur modified with dicyclopentadiene is particularly preferably used.

The amount of the sulfur modifier to be added is usually from 0.1 to 50 percent by mass, preferably from 0.5 to 20 percent by mass, based on the mass of sulfur. The content of the sulfur modifier gives an influence on the characteristics such as incombustibility, water shielding properties, and resistance to sulfur oxidizing bacteria, of the sulfur binder and the sulfur material containing the same. In general, the more sulfur modifier content can improve the

characteristics more. However, since the improving effect is limited with the content of about 10 percent by mass and is less in change with the content of more than 10 percent by mass, the improvement of characteristics are substantially satisfied with the use of the sulfur-modifying agent of 1 to 10 percent by mass. Therefore, the content of the sulfur modifier is more preferably from 1 to 10 percent by mass. The sulfur modifier of more than 10 percent by mass would add viscous properties to the elasticity of the resulting sulfur material which, therefore, has viscoelasticity. Furthermore, the sulfur modifier of more than 50 percent by mass would remarkably increase the viscoelasticity. On the other hand, the sulfur modifier of less than 0.1 percent by mass would result in a sulfur material with poor strength.

The modification of sulfur is firstly conducted by heating and melting sulfur. Further heating of sulfur in a solid state to a temperature of 119 °C initiates a phase change of from solid to liquid. Thereafter, a reaction is conducted by further heating the liquid sulfur to a reaction temperature with stirring the whole liquid sulfur and observing the viscosity with a suitable viscometer such as a

Brookfield type viscometer. The viscosity is preferably within the range of 0.05 to 1.2 Pa·s at 140 °C. However, the viscosity is more preferably within the range of 0.08 to 0.5 Pa·s with the objective of the strength of a molded article produced from the sulfur binder and workability during the production processes. The reaction temperature is determined to a certain range depending on the type of sulfur modifier. For example, in the case of using dicyclopentadiene, the reaction temperature is usually from 135 to 155 °C. The sulfur modifier may be added before or after sulfur is heat-melted. However, in the case of adding the sulfur modifier after melting sulfur, the pre-heated modifier is preferably added thereto. The modified sulfur used in the present invention after falling within the above-described viscosity range is preferably cooled to a temperature below the reaction temperature, generally 135 °C or lower so as not to be of high viscosity.

When the modified sulfur is prepared, the polymerization of sulfur and the sulfur modifier is preferably conducted in a sealed stirring vessel. The polymerization conducted in this vessel can prevent evaporation loss of the sulfur modifier due to heat

generated from the melted sulfur and thus can reduce the content of the sulfur modifier with respect to sulfur. Therefore, when the modified sulfur is prepared by this method, the characteristics of the sulfur material can be effectively improved even though the content of the sulfur modifier to sulfur is reduced to from 0.1 percent by mass or more to less than 2 percent by mass. Whereas, when the modified sulfur is prepared without using a sealed stirring vessel, it is preferable to blend the sulfur modifier such that the content thereof will be 2 percent by mass or more in order to improve sufficiently the characteristics of the sulfur material even though the above-described evaporation loss of sulfur occurs. The sealed stirring vessel may not be used after sulfur begins a reaction with the sulfur modifier and becomes a modified sulfur because no more evaporation loss of the sulfur modifier occurs.

Mixers which can be used in the present invention may be any of those as long as they can mix sufficiently but are preferably those for mixing liquid. For example, there may be used internal mixers, roll mills, drum mixers, pony mixers, ribbon mixers, homomixers, and static mixers. These mixers are preferably of

sealed type.

The sulfur binder used in the present invention may contain other materials to an extent that the achievement of purposes of the present invention is not bothered. Examples of such materials include heavy metal sequestering stabilizers such as sodium silicate, sodium sulfide, and chelating agent, asphalt, nickel sulfate, cobalt sulfate, silver sulfate, and various polymers. The content of these materials is preferably 30 percent by mass or less, based on the total mass of the sulfur binder.

Component (B), i.e., inorganic material used in the present invention contains chlorides at a high chloride concentration which is from 0.02 to 10 percent by mass, preferably from 1.0 to 10 percent by mass.

Component (B) is preferably comprised of (B-1) a high chloride concentration inorganic material of a chloride concentration of 0.02 to 25 percent by mass and (B-2) a low chloride concentration inorganic material of a chloride concentration of less than 0.02 percent by mass. In this case, the chloride concentration of Component (B-1) may exceed 10 percent by mass as long as the chloride concentration of

Component (B) comprised of Components (B-1) and (B-2) is within the range of 0.02 to 10 percent by mass.

Component (B-1) may not be suitable for concrete aggregates due to its too high chloride concentration or may have a particle size and strength resulting from granulation by a treatment using the sulfur binder, unsuitable for aggregates. Therefore, Component (B-1) is preferably mixed with Component (B-2) of a chloride concentration of less than 0.02 percent by mass. In such a case, Component (B-2) preferably contains another inorganic material capable of producing a granulated product with a particle size and strength suitable for aggregates.

No particular limitation is imposed on Component (B-1) as long as it is an inorganic material with a high chloride concentration which is within the range of 0.02 to 25 percent by mass, preferably 0.1 to 10 percent by mass, and more preferably 0.5 to 5 percent by mass. For example, Component (B-1) may be one or more inorganic materials selected from the group consisting of incinerated ash, incinerated fly ash, and melted fly ash generated from a municipal waste high temperature melting furnace.

Incinerated ash is exhausted from various combustion furnaces such as incineration furnaces for municipal wastes and industrial wastes and contains oxides such as silica, alumina, calcium oxide, and iron oxide as main components but also contains toxic metals such as lead, cadmium, and arsenic in a large amount. Therefore, incinerated ash has been used for landfill disposal at a final disposal site which does not discharge sewage water.

No particular limitation is imposed on Component (B-2) as long as it is an inorganic material of a low chloride concentration which is less than 0.02 percent by mass. For example, Component (B-2) may be one or more inorganic materials selected from the group consisting of coal ash exhausted from electric power plants and general industries, fluidized sand used in fluidized-bed incinerators, polish chips, by-products resulting from the production of various metals, such as steel slag and dust, ferronickel slag, aluminum dross, and copper slag.

Coal ash is discharged from various coal fired combustion furnaces for electric power generation or heating and utilized as a mixing material for concretes and civil engineering materials.

Steel slag is a slug by-produced from iron manufacturing industries and includes blast furnace slag discharged from a blast furnace, open hearth furnace slag discharged from an open hearth furnace, and converter slag discharged from a steel converter. The main components of steel slag are oxides such as silica, alumina, calcium oxide, and iron oxide and other inorganic sulfides.

Component (B-1) is blended in an amount of 40 to 100 percent by mass, preferably 45 to 80 percent by mass, and more preferably 50 to 70 percent by mass, based on the total mass of Component (B). Component (B-2) is blended in an amount of 0 to 60 percent by mass, preferably 55 to 20 percent by mass, and more preferably 50 to 30 percent by mass, based on the total mass of Component (B). Particularly preferred Components (B) are those comprised of incinerated ash as Component (B-1) and steel slag and/or coal ash as Component (B-2) and having a chloride concentration of 0.02 to 10 percent by mass. Such Component (B) can be used effectively in the present invention.

When the chloride concentration of Component (B) is 0.02 to 10 percent by mass, elution of chlorides to

the outside of the system can be suppressed to a stipulated value or less by the method of the present invention. More specifically, the sulfur material produced by the method of the present invention can be significantly decreased in the chloride elution amount measured by a test of chloride content in fine aggregates for concrete or mortar (Mohr's method) defined by the Japan Society of Civil Engineering. Even after 120-hour extraction time, the chloride elution amount of the sulfur material can be less than 0.1 percent by mass, preferably less than 0.06 percent by mass.

The term "chloride" used herein is an inorganic chloride which could deteriorate concrete and denotes sodium chloride, potassium chloride, calcium chloride, and magnesium chloride.

The sulfur material of the present invention is obtained by melting and mixing (A) 10 to 50 percent by mass, preferably 10 to 30 percent by mass of a sulfur binder and (B) 50 to 90 percent by mass, preferably 70 to 90 percent by mass of an inorganic material of a chloride concentration of 0.02 to 10 percent by mass and granulating the melted mixture thereby covering the inorganic material with the sulfur binder. This sulfur

material of the present invention is preferable for civil engineering and construction materials and can be used suitably for various aggregates for concrete, mortar, roadway subgrade, fillers for caissons, landfill materials, and banking materials.

Melting and mixing are preferably conducted at a temperature of 135 to 155 °C such that the components are well-mixed. Upon melting and mixing, it is preferable that Component (B) preheated at a temperature of 125 to 155 °C and Component (A) heated and melted at a temperature of 125 to 155 °C are charged almost at the same time into a mixer preheated at a temperature of 135 to 155 °C.

Melting and mixing time varies depending on Components (A) and (B) but is from 5 minutes to 5 hours. Particularly, when Component (A) is a modified sulfur, melting and mixing time varies greatly depending on whether or not the modified sulfur is produced simultaneously with the melting and mixing. For example, in the case of using a modified sulfur prepared beforehand as the sulfur binder (including a mixture of a modified sulfur and sulfur), melting and mixing time is from 5 minutes to 30 minutes. Although the melting and mixing is completed in a short period of

time because the fluidity of the modified sulfur is higher and the mixing efficiency is more enhanced when the melting and mixing temperature is 155 °C or lower but still high, a curing reaction progresses at such a high temperature. Whereas, at a low temperature, the fluidity of the modified sulfur is decreased, but the curing reaction progresses slowly. Therefore, it is preferable that the mixer is preheated at a temperature within the range of 140 to 145 °C and melting and mixing is conducted at a temperature within the range of 140 to 145 °C because at a temperature within these ranges the components can be well-mixed for 5 to 30 minutes.

Mixing time is desirously as short as possible so as to avoid the curing reaction, to an extent that the properties of the resulting product are not adversely affected. A too short mixing time fails to mix the sulfur binder and the inorganic material sufficiently, and thus the resulting molded article or granulated product does not have a continuous phase with some voids formed therein and has a rough surface. When the components are stirred sufficiently while being mixed, the resulting molded article or granulated product exhibits a completely continuous phase and has a smooth surface.

With the objective of easy handling, Components (A) and (B) are preferably mixed with maintaining the viscosity at 140 °C of Component (A) in the optimum range of 0.05 to 1.2 Pa · s. A sulfur binder with a viscosity at 140 °C of less than 0.05 Pa · s could lack binding power due to the absorption to the inorganic material and thus degrade the performance characteristics of the resulting material. A sulfur binder with a viscosity at 140 °C in excess of 1.2 Pa · s is extremely decreased in fluidity and also in workability and deteriorates wetting with the inorganic material. When a modified sulfur is used, it requires careful handling upon production because the viscosity could increase with lapse of time.

Any mixer may be used as long as it can mix Components (A) and (B) sufficiently. For example, a solid-liquid stirring mixer may be used. More specifically, there may be used internal mixers, roll mills, drum mixers, screw extruders, pug mills, pony mixers, and ribbon mixers.

In the production of the sulfur material of the present invention, after the sulfur binder is prepared and solidified by chilling, it may be re-melted and then mixed with the inorganic material. Alternatively, the

sulfur binder just prepared may be mixed with the inorganic material before chilled and solidified.

When the unsolidified sulfur binder is mixed with the inorganic material, the sulfur binder may be mixed or pre-mixed with the inorganic material after or before the binder has a viscosity within an optimum range. However, in either of the cases, the reaction time or temperature is preferably controlled such that the optimum viscosity of the sulfur binder is finally obtained.

Alternatively, in the case of using a modified sulfur as the sulfur binder in the present invention, sulfur may be modified with a sulfur modifier before being mixed with the inorganic material or while being melted and mixed therewith.

No particular limitation is imposed on a method of granulating the melted mixture. Examples of the method include those wherein the melted mixture is granulated while being solidified by chilling to be formed into a granulated product and wherein a molded article obtained by solidifying the melted mixture by chilling is pulverized thereby obtaining a granulated product.

Granulation is preferably conducted by a rolling

or vibration granulation method using a rolling or vibration granulator equipped with a normal drum and a horizontal or inclination plate.

Specific conditions for these methods are arbitrarily selected depending on the types or blend ratio of Components (A) and (B) such that the resulting granulated product has a particle size suitable for aggregates for concrete or mortar. The specific conditions are preferably set such that the methods can produce particles with a size of generally 2 to 44.4 mm measured using a JIS standard sieve. The particle size is arbitrarily selected depending on the usage of the final product.

The rolling granulation method can adjust the particle size of a granulated product by changing the inclination angle or rotation speed of the rotary plate or the drum. However, it is not necessary to select the sizes of the rotary plate and the drum in view of a desired particle size. For example, particles with an arbitrary size within the range of 2 to 44.4 mm can be produced by changing the inclination angle of the rotary plate. The inclination angle is generally adjusted within the range of 0 to 70 degrees.

The vibration granulation method can adjust the particle size of a granulated product by changing the

frequency or amplitude of vibration and the inclination angle. For example, the frequency, amplitude, and time of vibration are selected to be 3,000 rpm, 0.3 mm or larger, and from 30 minutes to 3 hours such that solidified sulfur in a melted state does not scatter. The inclination angle is adjusted within the range of 0 to 60 degrees. The vibration mode may be a reciprocal mode, a rotation mode, or a mixed mode thereof. The granulated product may also be obtained by actually vibrating the melted mixture using a rotary drum.

Although the granulated product may be obtained by cracking the molded article, it is difficult to produce the particles with an arbitrary size. Therefore, the granulation methods are preferably used. If necessary, the granulated product resulting from cracking may be sieved so as to obtain a particle size distribution suitable for aggregates for concrete or mortar.

As an alternative, there is a method wherein melted sulfur is dropped in water. However, this method is not preferable because the inorganic material fails to cover the sulfur binder, resulting in elution of heavy metals in the water and formation of rust on the granulated product.

The average particle size of the sulfur material

of the present invention is within the range of preferably 2 to 20 mm, more preferably 2 to 10 mm, and further more preferably 2 to 8 mm.

The compressive strength of the sulfur material of the present invention is usually from 10 to 100 Pa, preferably from 20 to 100 Pa, and more preferably from 30 to 100 Pa.

[Brief Description of the Drawing]

Fig. 1 is a graph indicating a relation between extraction time and chloride concentration.

[Best Mode for Carrying out the Invention]

Hereinafter, the present invention will be described in more details by way of the following examples, which should not be construed as limiting the scope of the invention.

The upper limit values of chlorides contained in concretes for civil engineering structures used in Examples (0.60 kg/cm^3 or 0.30 kg/cm^3 in Table 1) are the total of chlorides contained in each material constituting fresh concretes. Such chloride-containing materials are fine aggregates, cement, water, admixtures, and the like. However,

chloride-free admixtures have been recently used. The maximum chloride content of portland cement is usually 0.015 percent. The chlorine content of tap water is limited to 200 ppm. Assuming that these materials, i.e., cement, water, and fine aggregates are mixed at a ratio of a unit amount of 350 kg/m³, a unit amount of 180 kg/m³, and a unit amount of 800 kg/m³, respectively, which ratio is typical for concrete, the permissible chloride amounts of the fine aggregates are found as shown in Table 2. That is, when the upper limit chloride values of the concretes intended for civil engineering structures are 0.60 kg/m³ and 0.30 kg/m³, the permissible chloride contents of the fine aggregates are 0.0639 percent and 0.0264 percent, respectively. Therefore, these values were used as reference values.

Table 1 Reference Values of Chlorine in a Fresh Concrete

Object	Application	Upper limit of Chloride kg/m ³	Permissible amount in the fine aggregate ¹⁾
Civil Engineering Structures	Prestressed concrete of conventional reinforced concrete - post-tensioning system, plain concrete having reinforcing bars	0.6	0.0639
	Prestressed concrete of pre-tensioning system, for grout alumina cement with no sheath, where electric corrosion could occur	0.3	0.0264
Building Structures	Conventional reinforced concrete	0.3	-
	High durability concrete	0.2	-

1) Each permissible amount was for the concrete wherein each of the cement, water, and aggregate is contained in a unit amount of 350 kg/m³, 180 kg/m³, and 800 kg/m³, using a normal portland cement.

Table 2 Permissible Chlorine Ion Concentration in the Aggregate
(Normal Portland Cement)

	Chloride concentration mass%	Blend ratio kg/m ³	Chloride content per unit kg/m ³
Cement	0.0150	350	0.053
Water	0.0200	180	0.036
Aggregate	0.0639	800	0.512
Upper limit content in the concrete (1)	-	-	0.600
Cement	0.0150	350	0.053
Water	0.0200	180	0.036
Aggregate	0.0264	800	0.212
Upper limit content in the concrete (2)	-	-	0.300

[Example 1]

A pre-dried blast furnace slag with a chloride concentration of 0 percent by mass was mixed with an incinerated ash with a chloride concentration of 2.8 percent by mass at a mix ratio of 5 : 4 thereby preparing (B) an inorganic material. To the resulting organic material was added sulfur in such amounts as to obtain mixtures whose sulfur contents are 19 percent by mass (Example 1a), 22 percent by mass (Example 1b), and 26 percent by mass (Example 1c), based on 100 percent by mass of a mixture of (A) the sulfur binder (sulfur) and (B) the inorganic material. These mixtures were melted and kneaded at a temperature of 150 °C thereby obtaining various types of melted mixtures (Examples 1a, 1b, and 1c).

1,000 g of each of the resulting mixtures were poured into a table-type vibrator (two HV-type vibrators manufactured by MURATA SEIKO Co., Ltd. were used and a 500 x 500 mm steel plate was fixed thereon as a vibration table) and solidified while being vibrated at a vibration frequency of 3000 times/minute and a vibration amplitude of 1 mm for a period of one minute thereby obtaining various types of granulated sulfur solids (sulfur materials). The maximum particle size of the resulting materials was 10 mm. The average particle sizes in Examples 1a, 1b, and 1c were 4 mm, 5 mm, and 6 mm, respectively.

Each of the resulting sulfur materials (Examples 1a, 1b, and 1c) was subjected to a test of chloride content in the aggregate for concrete and mortar (Mohr's method) prescribed by the Japan Civil Engineering Society to measure the amount of the eluted chlorides. The measurements were conducted at intervals of 1, 3, 6, 12, 120, and 140 hours in order to confirm that the amount of the eluted chlorides does not change with lapse of time. The results are shown in Table 3 and Fig. 1.

As shown in Table 3 and Fig. 1, in either of Examples, the amount of elution reached to the maximum after about 100 hours, and no further increase was

observed. No further chloride more than that observed after 120 hours was eluted. Furthermore, in either of Examples, these amounts of elution were significantly lower than 2.8 percent by mass of the chloride ion content in the incinerated ash which is a material and satisfied the reference value of 0.064 percent by mass for a conventional reinforced concrete.

Table 3 Chloride Ion Concentration in Sulfix Granulated Matters (Mohr's Method)

Sample		Example 1a (19%)	Example 1b (22%)	Example 1c (26%)	Example 2 (19%)	Incinerated ash
Blend Ratio	mass%					
Sulfur		19.0	22.0	26.0	19.0	-
Incinerated ash		45.0	44.2	41.1	45.0	100.0
Blast furnace slag		36.0	33.8	32.9	36.0	-
Additive	mass% (s)	-	-	-	DCPD 5%	-
Chloride Concentration	mass%					
Extraction time	1h	0.008	0.006	0.005	0.006	-
	3h	0.010	0.007	0.006	0.007	-
	6h	0.011	0.008	0.008	0.008	-
	12h	0.016	0.011	0.011	0.011	-
	120h	0.060	0.044	0.039	0.043	-
	140h	0.059	0.044	0.039	0.042	-
Chloride Concentration	mass%	-	-	-		2.8

[Example 2]

190 g of a reacted polymer of 95 percent by mass of sulfur and 5 percent by mass of dicyclopentadiene were melted at a temperature of 150 °C and kneaded with 450 g of a pre-dried blast furnace slag with a chloride concentration of 0 percent by mass and 360 g of an

incinerated ash with a chloride concentration of 2.8 percent by mass. 1,000 g of the resulting mixture were poured into a table-type vibrator (two HV-type vibrators manufactured by MURATA SEIKO Co., Ltd. were used and a 500 x 500 mm steel plate was fixed thereon as a vibration table) and solidified while being vibrated at a vibration frequency of 3,000 times/minute and a vibration amplitude of 1 mm for a period of one minute thereby obtaining a granulated sulfur solid (sulfur material). The maximum and average particle sizes of the resulting material were 10 mm and 5 mm, respectively.

The resulting sulfur material was subjected to a test of chloride content in the aggregate for concrete and mortar (Mohr's method) prescribed by the Japan Civil Engineering Society to measure the amount of the eluted chlorides. The measurements were conducted at intervals of 1, 3, 6, 12, 120, and 140 hours in order to confirm that the amount of the eluted chlorides does not change with lapse of time. The results are shown in Table 3 and Fig. 1.

As shown in Table 3 and Fig. 1, similarly to the Examples using sulfur as the binder, the amount of elution reached to the maximum after about 100 hours, and no further increase was observed. No further

chloride more than that observed after 120 hours was eluted. Furthermore, the amount of elution was 0.042 percent by mass which was significantly lower than 2.8 percent by mass of the chloride ion content in the incinerated ash which is a material. The amount was also less by 30 percent than 0.059 percent by mass for using sulfur as the binder and satisfied the reference value of 0.064 percent by mass for a conventional reinforced concrete.

[Example 3]

A pre-dried blast furnace slag with a chloride concentration of 0 percent by mass was mixed with an incinerated ash with a chloride concentration of 2.8 percent by mass at a mix ratio of 5 : 4. To the resulting material was added sulfur in such an amount as to obtain a mixture whose sulfur content was 19 percent by mass, based on 100 percent by mass of total of sulfur and the material. The resulting mixture was melted and kneaded at a temperature of 150 °C thereby obtaining a melted mixture. 1,000 g of the resulting mixture was poured into a table-type vibrator (two HV-type vibrators manufactured by MURATA SEIKO Co., Ltd. were used and a 500 x 500 mm steel plate was fixed thereon as a vibration table) and solidified while being vibrated

at a vibration frequency of 3,000 times/minute and a vibration amplitude of 1 mm for a period of one minute thereby obtaining a granulated sulfur solid (sulfur material). The maximum and average particle sizes of the resulting material were 10 mm and 4 mm.

A concrete was produced using the material thus obtained as an aggregate instead of a ballast, and the strength of the concrete was measured. For preparation of the concrete, two methods were used one of which was a conventional method wherein the sulfur material as an aggregate was mixed with a mixture of cement and water and the other of which was a dry mix method wherein cement and the sulfur material were mixed beforehand and then mixed with water.

After the resulting concrete samples were aged for 28 days, the compressive, tensile, and flexural strengths were measured and compared with those of a normal concrete. The results are shown in Table 4. It was confirmed that the strengths of the concrete obtained by both the conventional method and the dry mix method were equivalent with or superior to those of a normal concrete.

Table 4 Study on Method of Producing Sulfix Aggregate Concrete

Type of aggregate		Ballast	Granulated sulfur solid		Standard
Mix method		Conventional mixing	Conventional mixing	Dry mixing	
Water-cement ratio (w/c)	%	58	58	58	-
Air content	%	4.5	4.6	4.5	4.5±1.5
Slump	cm	11.5	8.0	9.0	5~12
Compressive Strength	MN/m ²	34.7	33.5	38.3	
Tensile Strength	MN/m ²	2.67	2.12	2.42	-
Flexural Strength	MN/m ²	7.28	7.03	8.04	-

[Example 4]

(Preparation of Modified Sulfur)

Sulfur and dicyclopentadiene were reacted at a reaction mix mass ratio of 99 : 1 (the content of dicyclopentadiene was 1 percent by mass) in a sealed stirring vessel at a temperature of 135 °C thereby obtaining a modified sulfur which was a reaction polymer.

A granulated sulfur solid (sulfur material) was obtained by the method of Example 2 except that the modified sulfur obtained above was used in the same amount. The maximum and average particle sizes of the sulfur material were 10 mm and 5 mm.

The amount of chlorides eluted from the sulfur material was measured in the same manner. The results are shown in Table 5.

Table 5

Blend ratio of Sulfur material		mass%
Modified sulfur		19.0
Incinerated ash		45.0
Blast furnace slag		36.0
Chloride concentration		mass%
Extraction time	1h	0.005
	3h	0.007
	6h	0.008
	12h	0.012
	120h	0.041
	140h	0.042

As apparent from the results of Table 5, the amount of the eluted chloride reached to the maximum after about 140 hours, and no further increase was observed. Furthermore, the amount of elution was 0.042 percent by mass which was significantly lower than 2.8 percent by mass of the chloride ion content in the incinerated ash which is a material. The amount was also less by 30 percent than 0.059 percent by mass for using sulfur as the binder of Example 1 and satisfied the reference value of 0.064 percent by mass for a conventional reinforced concrete.

[Applicability in the Industry]

The method of the present invention can cover materials containing large quantities of chlorides such as sodium chloride or inorganic materials, typically industrial wastes such as incinerated ash,

with a sulfur binder and thus can suppress elution of the chlorides such that those materials can be used as aggregates for concrete. Therefore, the present invention can solve a problem related to lack of aggregate for concrete production and makes it possible to reduce cost, facilities, or time and use the wastes efficiently.

CLAIMS

1. A method for producing a sulfur material wherein (A) 10 to 50 percent by mass of a sulfur binder and (B) 50 to 90 percent by mass of an inorganic material with a chloride concentration of 0.02 to 10 percent by mass are melted and mixed at a temperature of 119 to 155 °C and the melted mixture is granulated.

2. The method according to claim 1 wherein (A) said sulfur binder is selected from the group consisting of sulfur; modified sulfurs obtained by adding to sulfur a sulfur modifier in an amount of 0.1 to 50 percent by mass and reacting the mixture by heating; and mixtures thereof.

3. The method according to claim 2 wherein said sulfur modifier is a material selected from the group consisting of olefinic hydrocarbons, diolefinic hydrocarbons, cycloolefinic hydrocarbons, and aromatic hydrocarbons, each having 4 to 20 carbon atoms.

4. The method according to claim 2 or 3 wherein said sulfur modifier is dicyclopentadiene.

5. The method according to any one of claims 1 to 4 wherein said Component (B) comprises (B-1) 40 to 100 percent by mass of an inorganic material with a chloride concentration of 0.02 to 25 percent by mass and (B-2) 0 to 60 percent by mass of an inorganic material with a chloride concentration of less than 0.02 percent by mass.

6. The method according to claim 5 wherein (B-1) said inorganic material with a chloride concentration of 0.02 to 25 percent by mass is incinerated ash and (B-2) said inorganic material with a chloride concentration of less than 0.02 percent by mass is steel slag and/or coal ash.

7. A sulfur material produced by the method according to any one of claims 1 to 6 used as aggregates for concrete or mortar.

8. A granulated sulfur material wherein (A) 10 to 50 percent by mass of a sulfur binder covers (B) 50 to 90 percent by mass of an inorganic material with a chloride concentration of 0.02 to 10 percent by mass.

9. The granulated sulfur material according to claim 8 wherein the average particle size is within the range of 2 to 20 mm.