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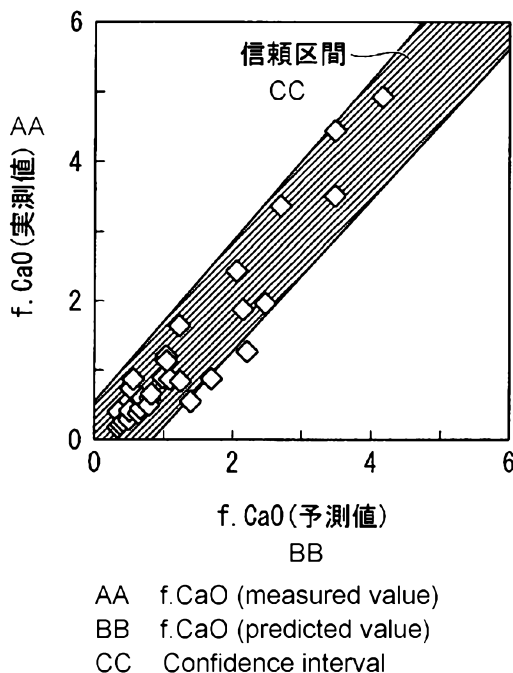
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[続葉有]

(54) Title: METHOD FOR CONTROLLING FREE LIME CONTENT OF CLINKER

(54) 発明の名称: クリンカ中の遊離石灰量を制御する方法



AA f. CaO (measured value)  
BB f. CaO (predicted value)  
CC Confidence interval

(57) Abstract: Provided is a method for controlling the free lime content of a clinker. This method comprises controlling the free lime content of a clinker so as to fall within a specified range, thereby minimizing cement-quality fluctuations which are dependent on the fluctuations in the free lime content. According to the method, the free lime content of a clinker is controlled by regulating the amount of sulfur trioxide resulting from fuel and the amount of a fluorine-containing mineralizer used in accordance to formulae (1) to (3):  $f\text{-CaO} = 0.29 \times e^{0.65 \times A}$  ( $A = a \times \text{SO}_3 + b$ ) (1)  $a = 0.0001 \times F + 9.2 \times t - 0.18 \times \text{HM} - 9.2$  (2)  $b = -0.0005 \times F - 32.8 \times t - 2.9 \times \text{HM} + 28.4$  (3) [wherein  $\text{SO}_3$  is the amount of sulfur trioxide in the clinker,  $a$  is a coefficient satisfying formula (2),  $b$  is a coefficient satisfying formula (3),  $F$  is the amount of fluorine in the clinker;  $t = X/1450$  (wherein  $X$  is a firing temperature ( $^{\circ}\text{C}$ )), and  $\text{HM}$  is a hydraulic modulus]

(57) 要約: クリンカ中の遊離石灰量を一定範囲内に収め、遊離石灰量の変動によるセメントの品質の変動を抑える、クリンカ中の遊離石灰量を制御する方法が提供される。そのようなクリンカ中の遊離石灰量を制御する方法は、燃料由来の三酸化硫黄量およびフッ素系鉱化剤の使用量を次式(1)~式(3)に従って調整することによって、クリンカ中の遊離石灰量 ( $f\text{-CaO}$ ) を制御する。  $f\text{-CaO} = 0.29 \times e^{0.65 \times A}$  ( $A = a \times \text{SO}_3 + b$ ) (1)  $a = 0.0001 \times F + 9.2 \times t - 0.18 \times \text{HM} - 9.2$  (2)  $b = -0.0005 \times F - 32.8 \times t - 2.9 \times \text{HM} + 28.4$  (3)  $\text{SO}_3$  は

クリンカ中の三酸化硫黄量、 $a$  は式(2)を満たす係数、 $b$  は式(3)を満たす係数、 $F$  はクリンカ中のフッ素量、 $t$  は焼成温度  $X^{\circ}\text{C}$  のとき  $t = X/1450$ 、 $\text{HM}$  は水硬率。



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(AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR,  
GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT,  
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— 国際調査報告 (条約第 21 条(3))

## DESCRIPTION

## Title of Invention

## METHOD FOR CONTROLLING FREE LIME CONTENT OF CLINKER

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## Technical Field

[0001]

The present invention relates to a method for controlling a free lime content of a clinker in a production method of cement so as to suppress cement quality fluctuation caused by the fluctuation of the free lime content.

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Priority is claimed on Japanese Patent Application No. 2012-077525, filed March 29, 2012, the content of which is incorporated herein by reference.

## Background Art

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[0002]

In cement plants, a mixed and ground substance consisting of limestone, clay, silica stone, iron ore, and the like is burned at a high temperature in an SP kiln or in an NSP kiln, thereby producing a hydraulic clinker. The free lime content of the clinker exerts an influence on physical properties of cement, and accordingly, the factories produce the clinker while controlling the free lime content to fall within a certain range.

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[0003]

Conventionally, as the method for controlling the free lime content, a method of varying the mixing ratio of respective raw materials (adjusting chemical components of a mixture of raw materials), the amount of raw materials put into the kiln, the rotation speed of the kiln, the length of flames of a burner, the amount of kiln exhaust gas to be

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aspirated, and the like or a method of using a mineralizer is used.

[0004]

For example, in the production method disclosed in PTL 1, the free lime content of the clinker and the like is controlled to be equal to or smaller than 0.5% by mass.

- 5 Moreover, in the method disclosed in PTL 2, the free lime content and the fluorine content of cement are controlled such that they satisfy a certain relational expression. Furthermore, PTL 3 discloses a production method which makes it possible to decrease the cement clinker burning temperature without increasing the amount of fluorine by causing the burned clinker to contain one or more elements selected from a group
- 10 consisting of fluorine, sulfur, chlorine, and bromine as well as one or more metal elements selected from a group consisting of group 3 to group 12 elements.

[0005]

However, there is a limit to control the free lime content by the above methods, and in the current situation, a great fluctuation of the free lime content is unavoidable.

- 15 When the free lime content fluctuates, the basic physical properties of cement (concrete), such as setting properties, strength, and fluidity, are influenced.

## Citation List

### Patent Literature

20 [0006]

[PTL 1] Japanese Unexamined Patent Application, First Publication No. 2008-285370

[PTL 2] Japanese Unexamined Patent Application, First Publication No. 2001-130932

25 [PTL 3] Japanese Unexamined Patent Application, First Publication No.

2011-207752

[0006a]

Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

Summary of Invention

Technical Problem

[0007]

The present invention provides a method for suppressing cement quality fluctuation caused by the fluctuation of the free lime content by controlling the free lime content of the clinker to fall within a certain range in a cement production process.

[0007a]

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

[0007a]

Unless the context clearly requires otherwise, throughout the description and the claims, the words “comprise”, “comprising”, and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”.

Solution to Problem

[0008]

According to the present invention, there is provided a method for controlling a free lime content that is constituted as below.

[1] A method for controlling a free lime content of a cement clinker, includes regulating the free lime content (f.CaO) in the cement clinker using Formulas (1) to (3).

$$f.CaO = 0.29 \times e^{0.65 \times A} (A = a \times SO_3 + b) \quad (1)$$

$$a = 0.0001 \times F + 9.2 \times t - 0.18 \times HM - 9.2 \quad (2)$$

$$b = -0.0005 \times F - 32.8 \times t + 2.9 \times HM + 28.4 \quad (3)$$

wherein in Formula (1), f.CaO is a free lime content (wt%),

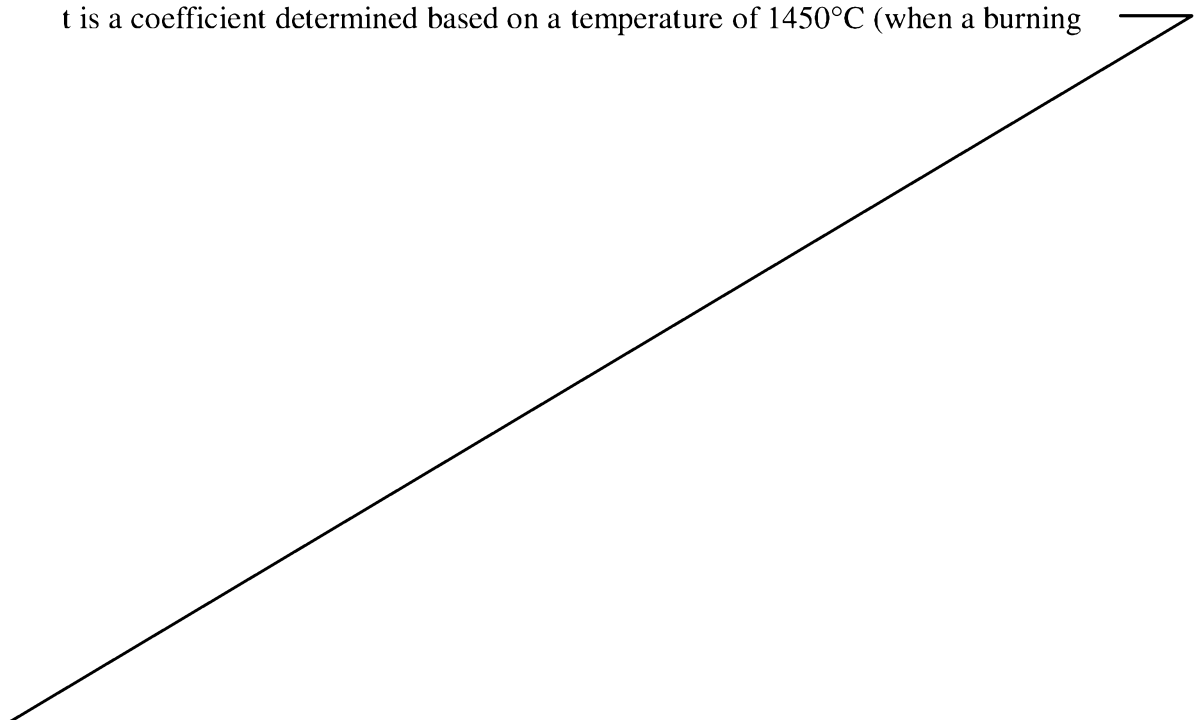
SO<sub>3</sub> is an amount (wt%) of sulfur trioxide in the cement clinker,

a is a coefficient satisfying Formula (2),

b is a coefficient satisfying Formula (3),

F is an amount (mg/kg) of fluorine in the cement clinker,

t is a coefficient determined based on a temperature of 1450°C (when a burning



temperature is  $X^{\circ}\text{C}$ ,  $t = X/1450$ ), and

HM is a hydraulic modulus.

[2] The method for controlling a free lime content of a cement clinker according to [1], the method may further include adjusting an additive amount of fluorite or

5 fluorine-containing waste that is a fluorine source in the cement clinker and used as a mineralizer, an used amount of fuel as an  $\text{SO}_3$  source in the cement clinker, and an additive amount of waste gypsum to control the free lime content (f.CaO) using the Formulas (1) to (3).

## 10 Advantageous Effects of Invention

[0009]

According to the control method of the present invention, it is possible to control the free lime content (f.CaO) of the clinker, by adjusting the used amount of fuel as an  $\text{SO}_3$  source in the clinker and the additive amount of waste gypsum, and by adjusting

15 the additive amount of fluorite or fluorine-containing waste that is a fluorine source in the clinker and used as a mineralizer using the Formula (1).

## Brief Description of Drawings

[0010]

20 FIG. 1 is a graph showing the correspondence between a calculated value of a free lime content and an actual measured value of the free lime content.

FIG. 2 is a graph showing the relationship between the  $\text{SO}_3$  amount and the fluorine amount at a burning temperature of  $1450^{\circ}\text{C}$ .

FIG. 3 is a graph showing the relationship between the  $\text{SO}_3$  amount and the

25 fluorine amount at a burning temperature of  $1350^{\circ}\text{C}$ .



FIG. 4 is a graph showing the relationship between the SO<sub>3</sub> amount and the fluorine amount at a burning temperature of 1300°C.

#### Description of Embodiments

[0011]

Hereinafter, the control method of the present invention will be described in detail based on embodiments.

The control method of the present invention is a method for controlling a free lime content of a cement clinker, in which the free lime content (f.CaO) of the clinker is regulated using Formulas (1) to (3).

$$f.CaO = 0.29 \times e^{0.65 \times A} \quad (A = a \times SO_3 + b) \quad (1)$$

$$a = 0.0001 \times F + 9.2 \times t - 0.18 \times HM - 9.2 \quad (2)$$

$$b = -0.0005 \times F - 32.8 \times t + 2.9 \times HM + 28.4 \quad (3)$$

[0012]

In Formula (1), f.CaO is a free lime content (wt%); SO<sub>3</sub> is the amount (wt%) of sulfur trioxide in the clinker; a is a coefficient satisfying Formula (2); b is a coefficient satisfying Formula (3); F is the amount (mg/kg) of fluorine in the clinker; t is a coefficient determined based on a temperature f 1450°C (when a burning temperature is X°C, t = X/1450); and HM is a hydraulic modulus.

[0013]

Most of SO<sub>3</sub>, which represents an amount of sulfur trioxide in the clinker, results from fuel for burning. Moreover, the SO<sub>3</sub> amount in the clinker is adjusted by intermixing waste gypsum board powder with fuel or by putting the waste gypsum board powder into a kiln from the kiln outlet part. The used amount of fuel or the amount of \_\_\_\_\_

waste gypsum put into the kiln is adjusted, it is possible to control the  $\text{SO}_3$  amount represented using Formula (1).

[0014]

Moreover, a mineralizer is added to the raw materials of the clinker. Fluorite, 5 fluorine-containing waste (sludge), and the like are used as the mineralizer. Fluorine contained in the clinker mainly results from the mineralizer. Accordingly, for example, by adjusting the additive amount of mineralizer, it is possible to regulate the coefficients a and b of Formulas (2) and (3) including the fluorine amount F and to finally control the  $\text{SO}_3$  amount in the clinker represented by Formula (1).

10 [0015]

The hydraulic modulus HM is an index represented by  $\text{HM} = \text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ . The greater the HM is, the amount of calcium oxide or alite in the clinker increases. As a result, burning reactivity decreases, hence the amount of free lime content increases. Generally, the hydraulic modulus HM of the raw material of the 15 clinker is 1.90 to 2.30.

[0016]

Furthermore, Formula (1) is satisfied when the fluorine amount F in the clinker is equal to or greater than 300 mg/kg. If the fluorine amount F in the clinker is smaller than this, the correlation between fluorine and  $\text{SO}_3$  tends to be weakened, and the free 20 lime content (f.CaO) of the clinker tends to increase greater than the value represented by Formula (1).

Examples

[0017]

Examples of the present invention will be described below.

25 The  $\text{SO}_3$  amount in the clinker was measured according to JIS R 5202:2010

“Methods for chemical analysis of cement”. The fluorine amount in the clinker was measured by X-ray fluorescence analysis (powder briquette method or bead method).

The free lime content (f.CaO) of the clinker was measured according to JCAS I-01:1997 “Quantification of free calcium oxide”.

- 5           The burning temperature coefficient  $t$  is a coefficient determined based on a temperature of 1450°C. When the burning temperature is 1350°C,  $t = 1350/1450 = 0.93$ , and when the burning temperature is 1450°C,  $t = 1450/1450 = 1.00$ .

[0018]

[Example 1]

- 10           The SO<sub>3</sub> amount, fluorine amount, and free lime content (f.CaO) of the produced cement clinker were measured. The results are shown in Table 1 together with the hydraulic modulus HM and the burning temperature coefficient  $t$ . Moreover, the free lime content (estimated f.CaO), which is calculated by plugging the hydraulic modulus of the raw material, the burning temperature coefficient, the measured SO<sub>3</sub> amount, and the
- 15           fluorine amount into Formula (1), is also shown in Table 1. In addition, the relationship between the free lime content (estimated f.CaO) based on Formula (1) and the actual measured free lime content (f.CaO) is shown in FIG. 1.

[0019]

- 20           As shown in Table 1, a difference between the free lime content (f.CaO) based on Formula (1) and the actual measured free lime content (f.CaO) is small and within a narrow range as shown in FIG. 1. This shows that Formula (1) showing the free lime content (f.CaO) of the clinker is highly reliable, and accordingly, it is possible to reliably control the free lime content (f.CaO) of the clinker based on Formula (1).

[0020]

- 25           [Example 2]

FIG. 2 and FIG. 3 show the relationship between the  $\text{SO}_3$  amount and the fluorine amount that make the free lime content (f.CaO) at each burning temperature fall within a range of  $0.5 < \text{f.CaO} < 1.0$  based on Formula (1) when each of the raw materials of the clinker having the hydraulic modulus HM of 1.9, 2.1, and 2.3 is burned at 1300°C, 5 1350°C, and 1450°C respectively. In the drawings, the shaded area is in a range of  $0.5 < \text{f.CaO} < 1.0$ . By adjusting the  $\text{SO}_3$  amount and the fluorine amount, it is possible to control the free lime content to fall within a range of  $0.5 < \text{f.CaO} < 1.0$ .

[0021]

[Table 1]

	SO <sub>3</sub>	F	t	HM	f.CaO	Estimated f.CaO		SO <sub>3</sub>	F	t	HM	f.CaO	Estimated f.CaO
Example 1	1.83	1160	1.00	1.89	0.18	0.30	Example 22	2.00	2700	0.90	2.10	0.63	0.80
Example 2	0.43	1015	1.00	1.89	0.21	0.38	Example 23	0.88	595	1.00	2.31	0.66	0.84
Example 3	0.84	2455	1.00	2.31	0.26	0.50	Example 24	3.15	2740	0.90	2.31	0.71	0.50
Example 4	2.64	2610	1.00	2.31	0.26	0.42	Example 25	2.72	695	1.00	2.30	0.74	0.56
Example 5	0.41	305	1.00	1.88	0.33	0.46	Example 26	1.12	2780	0.93	2.31	0.82	1.23
Example 6	1.83	1150	0.93	1.90	0.36	0.64	Example 27	3.05	1580	0.93	2.31	0.84	0.57
Example 7	2.11	340	1.00	1.89	0.38	0.35	Example 28	0.50	5000	0.90	2.10	0.86	1.10
Example 8	2.00	5000	0.93	2.10	0.39	0.36	Example 29	1.10	1595	0.93	2.31	0.87	1.71
Example 9	1.62	2535	1.00	2.31	0.39	0.46	Example 30	2.07	1565	0.93	2.31	0.87	1.00
Example 10	3.05	2370	0.93	2.30	0.41	0.51	Example 31	2.00	1390	0.90	2.10	1.14	1.06
Example 11	2.09	340	0.93	1.91	0.43	0.66	Example 32	2.12	2700	0.90	2.30	1.20	1.03
Example 12	1.72	1450	1.00	2.30	0.46	0.58	Example 33	0.50	620	0.93	2.10	1.25	2.21
Example 13	2.62	1605	1.00	2.30	0.46	0.49	Example 34	2.00	655	0.93	2.31	1.63	1.25
Example 14	0.84	1625	1.00	2.30	0.49	0.63	Example 35	1.10	675	0.93	2.30	1.86	2.17
Example 15	2.01	2670	0.93	2.30	0.49	0.81	Example 36	0.50	2310	0.90	2.10	1.95	2.49
Example 16	2.00	2440	0.93	2.10	0.50	0.61	Example 37	1.15	2650	0.90	2.31	2.41	2.09
Example 17	0.50	5000	0.93	2.10	0.50	0.58	Example 38	1.15	1635	0.90	2.31	3.39	2.71
Example 18	2.00	5000	0.90	2.10	0.55	0.50	Example 39	0.50	1195	0.90	2.10	3.52	3.50
Example 19	2.00	1340	0.93	2.10	0.56	0.77	Example 40	1.16	670	0.90	2.30	4.44	3.45
Example 20	1.73	645	1.00	2.31	0.56	0.70	Example 41	0.50	640	0.90	2.10	4.89	4.15
Example 21	0.43	1020	0.93	1.90	0.56	1.41							

Note: SO<sub>3</sub> is an SO<sub>3</sub> amount (wt%) in the clinker; F is a fluorine amount (mg/kg) in the clinker; t is a coefficient determined based on a burning temperature (1.00 = 1450/1450, 0.93 = 1350/1450); f.CaO is an actual measured value (wt%); and Estimated f.CaO is a value calculated (wt%) based on Formula (1).

## Industrial Applicability

[0022]

The present invention can be applied to a method for controlling the free lime content (f.CaO) of the clinker by adjusting the used amount of fuel as an SO<sub>3</sub> source in  
5 the clinker, the additive amount of waste gypsum, and adjusting the additive amount of fluorite or fluorine-containing waste that is a fluorine source in the clinker and used as a mineralizer using the Formula (1).

## CLAIMS

1. A method for controlling a free lime content of a cement clinker, comprising:  
regulating the free lime content (f.CaO) of the cement clinker using Formulas (1) to (3).

$$f.CaO = 0.29 \times e^{0.65 \times A} \quad (A = a \times SO_3 + b) \quad (1)$$

$$a = 0.0001 \times F + 9.2 \times t - 0.18 \times HM - 9.2 \quad (2)$$

$$b = -0.0005 \times F - 32.8 \times t + 2.9 \times HM + 28.4 \quad (3)$$

wherein in Formula (1), f.CaO is a free lime content (wt%),

SO<sub>3</sub> is an amount (wt%) of sulfur trioxide in the cement clinker,

a is a coefficient satisfying Formula (2),

b is a coefficient satisfying Formula (3),

F is an amount (mg/kg) of fluorine in the cement clinker,

t is a coefficient determined based on a temperature of 1450°C (when a burning temperature is X°C,  $t = X/1450$ ), and

HM is a hydraulic modulus.

2. The method for controlling a free lime content of a cement clinker according to Claim 1, further comprising:

adjusting an additive amount of fluorite or fluorine-containing waste that is a fluorine source in the cement clinker and used as a mineralizer, an used amount of fuel as an SO<sub>3</sub> source in the cement clinker, and an additive amount of waste gypsum to control the free lime content (f.CaO) using the Formulas (1) to (3).

FIG. 1

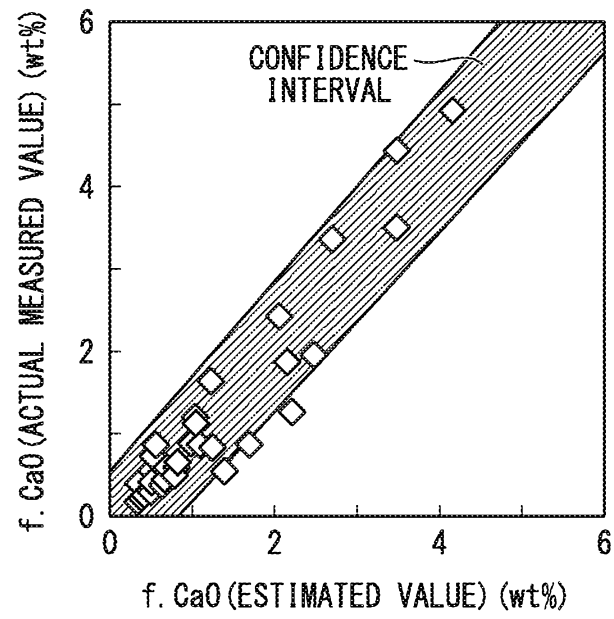




FIG. 2

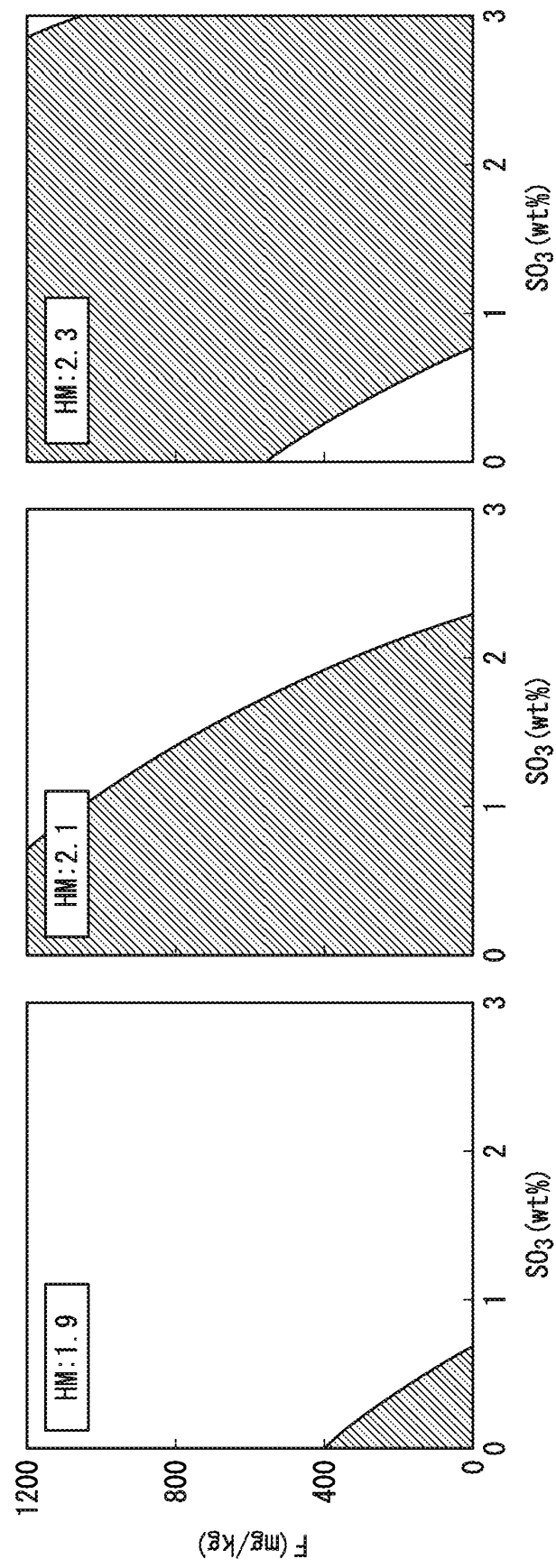


FIG. 3

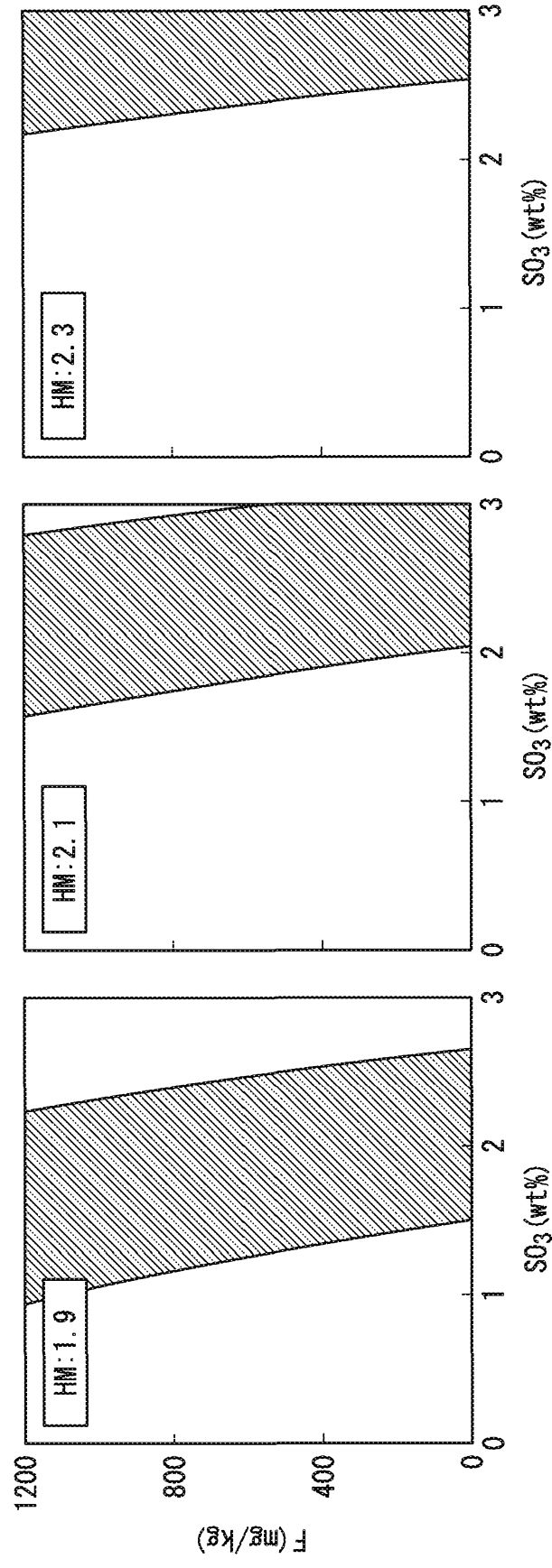


FIG. 4

