# (19) Japanese Patent Office (JP)

(11) Laid Open Patent Application No.

# (12) Unexamined Patent Application Bulletin (A)

1-304100

(51) Int. Cl.<sup>4</sup> Identification Code

Internal File No.

(43) Publication Date

C 02 F 9/00

Z-7308-4D

December 7, 1989

# Examination Request not yet made Number of Claims 1 (Total 4 pages)

(54) **Title of the Invention:** Device for treating desulfurization wastewater from wet flue gas

desulfurization device

(21) **Application No.:** 63-134679

(22) **Application Date:** June 1, 1988

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# **Specification**

# 1. Title of the Invention

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Device for treating desulfurization wastewater from wet flue gas desulfurization device

## 2. Claims

(1) In a device for treating desulfurization wastewater from a wet flue gas desulfurization device that absorbs and removes sulfur oxides in flue gas with an absorbent slurry, the device for treating desulfurization wastewater from a wet flue gas desulfurization device characterized by comprising: a heavy metal removal device in which coal combustion ash (fly ash) is added to desulfurization wastewater to remove heavy metal components and/or fluorine components; a COD treatment device that performs COD treatment of treated wastewater discharged from said device; and a nitrogen compound removal device that removes nitrogen compounds in this COD-treated wastewater.

# 3. Detailed Description of the Invention [Field of Industrial Application]

The present invention relates to a device for treating desulfurization wastewater from a wet flue gas desulfurization device, and in particular relates to a device for treating desulfurization wastewater from a wet flue gas desulfurization device, which is suitable for removing heavy metal components and the like in this wastewater.

[Prior Art]

Generally, when coal or petroleum is burned, the flue gas produced contains sulfur oxides, nitrogen oxides and the like, which cause air pollution. For this reason, treatment for sulfur oxides is performed with a wet flue gas desulfurization device, in order to remove these harmful substances from flue gases, and in conjunction therewith desulfurization wastewater is discharged from the wet flue gas desulfurization device. Because this desulfurization wastewater contains suspended matter, heavy metals, inorganic ions, organic matter and the like, which contaminate the environment and cause various sorts of damage, it cannot be discharged directly.

FIG. 2 shows an example of a wastewater treatment system for a wet flue gas desulfurization device in a coal-fired thermal power plant. Desulfurization wastewater 1 is accumulated in a water storage tank 2. Next, slaked lime 6 is added in a reaction tank 101, and an aggregating agent 102 is further added before this is sent to a settling tank 103, where fluorine settles and is removed. Caustic soda 105 and an aggregating agent 106 are further added in a pH-adjustment, oxidation and aggregation tank 104, heavy metals are settled and removed in a settling tank 107, and this passed through a filter 108. This [filtrate] contains dithionate  $(S_2O_6^{2-})$ ,

which is produced in the absorption tower and, as this is a cause of COD, it must be removed. To remove dithionate, the pH is adjusted by adding sulfuric acid 110 to the pH adjustment tank 109, after which this passes through a COD removal tower 111, and is neutralized by adding caustic soda 13 in a neutralization tank 112. As a result of these treatments for fluorine, heavy metals and COD, the treated wastewater 11 satisfies wastewater standards of no greater than 10 to 15 mg/l for SS and COD, no greater than 15 ppm for fluorine, and no greater than 1 ppm for oils.

Note that the aforementioned wastewater contains some amount of nitrogen compounds. This is mainly the result of absorbing some (approximately 1 to 2%) of the NOx in the gas (mostly NO and a small amount of NO<sub>2</sub>), and thus this is principally in the form of nitrates but small amounts of compounds containing nitrogen and sulfur such as imidodisulfonic acid are also included. Normally, the nitrogen concentration of the treated wastewater 11 is no greater than 500 ppm, and running a nitrogen treatment system 10 allows the nitrogen concentration of the treated wastewater 11 to be reduced to no greater than 10 ppm.

Meanwhile, coal ash collected with an electric precipitator in a coal-fired thermal power plant, which is to say fly ash, is advantageously used in cement, building materials, fertilizer, soil conditioners and the like, but it is a fact that the majority must be disposed of in landfills. In the case of landfill disposal, because the water that leaches from the fly ash is alkaline, it is necessary to consider the impact on the surrounding environment.

### [Problems to Be Solved by the Invention]

In the conventional art such as described above, it was necessary to consider the impact on the surrounding environment, because the water that leaches from the fly ash is primarily alkaline. Furthermore, there were problems in so much as caustic soda and slaked lime were added in order to remove heavy metals and fluorine in the desulfurization wastewater, and thus operational costs increased due to the cost of these chemicals, and there was a need for chemical storage facilities and the like.

An object of the present invention is to remove heavy metals and fluorine without adding caustic soda or slaked lime, or with reduced amounts added.

# [Means for Solving the Problems]

In a device for treating desulfurization wastewater from a wet flue gas desulfurization device that absorbs and removes sulfur oxides in flue gas with an absorbent slurry, these problems in the conventional art described above are solved by a device for treating desulfurization wastewater from a wet flue gas desulfurization device characterized by comprising: a heavy metal removal device in which

coal combustion ash (fly ash) is added to desulfurization wastewater to remove heavy metal components and/or fluorine components; a COD treatment device that performs COD treatment of treated wastewater discharged from said device; and a nitrogen compound removal device that removes nitrogen compounds in this COD-treated wastewater.

# [Examples]

FIG. 1 shows an example of a desulfurization wastewater treatment device according to the present invention.

In FIG. 1, desulfurization wastewater 1 from a wet flue gas desulfurization device is accumulated in a water storage tank 2. Next, this is sent to a heavy metal removal device 150. Specifically, this is sent to a reaction tank 3, and fly ash 5 is added so that the pH value of the reaction tank 3 becomes 6 to 8, according to a pH meter 12. In the event that the pH value does not rise to the predetermined value when the fly ash 5 is added, slaked lime 6 may also be added to the fly ash 5. Before this is sent to a settling tank 4, an aggregating agent 102 is added, and heavy metals hydroxides and fluorine compounds that have settled are discharged as sludge 7 from the bottom of the settling tank 4. This sludge 7 can be used as a landfill material or the like, after dewatering. Supernatant water 8 in the settling tank 4 is sent to a COD treatment device 9, and after removing COD, this is sent to a nitrogen compound treatment device 10 where nitrogen components are removed. The treated wastewater 11, after the removal of nitrogen components has been completed, is discharged or reused.

The fly ash 5 from the coal-fired thermal power plant includes, as principal components, silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), quick lime (CaO) and the like. The quick lime content is approximately 1 to 10%, and this reacts with water to form slaked lime (Ca(OH)<sub>2</sub>) and calcium carbonate (CaCO<sub>3</sub>). The reason the pH value increases when the fly ash 5 is added to the wastewater is because it contains quick lime (CaO). Depending on the type of coal, the quick lime content in the fly ash may be low, such that it may be difficult to adjust the pH of the wastewater,

and therefore the system is configured so that slaked lime  $(Ca(OH)_2)$  can be supplementally added to the fly ash.

The experiment described next was performed based on the present invention, and confirmed the effects of the present invention.

The composition of the test desulfurization wastewater provided to the experiment is as follows.

pH: 1.2 SS: 7600 mg/l CI:: 3700 mg/l F:: 620 mg/l Na<sup>+</sup>: 2700 mg/l Mg<sup>2+</sup>: 615 mg/l Ca<sup>2+</sup>: 306mg/l Fe<sup>2</sup>: 132 mg/l Al<sup>3+</sup>: 47mg/l

# **Experimental Example 1**

The wastewater described above, in the amount of 1 liter, was collected in a beaker and, while gently magnetically stirring, fly ash recovered from the same power plant was added so as to produce a pH of 7.0, and stirring was continued for approximately 10 minutes. Subsequently, stirring was stopped and this was left to stand for approximately 30 minutes, and when the supernatant at the top of the beaker was then sampled and analyzed, the F-concentration was 6 mg/l, the Fe<sup>2+</sup> concentration was 1 mg/l or less, and the Al<sup>3+</sup> was 2 mg/l.

# **Comparative Example 1**

When  $Ca(OH)_2$  was used in place of the fly ash added in Example 1, and from that point onward the same operations were performed, the F-concentration was 27 mg/l, the Fe<sup>2+</sup> concentration was 1 mg/l or less, and the  $Al^{3+}$  was 2 mg/l.

From these results, it was found that, with Ca(OH)<sub>2</sub> alone, the F- remained in the solution, and the removal rate was poor.

### **Experimental Example 2**

When the same operations were performed using a mixture in which fly ash and slaked lime were mixed at a ratio of 1:1, in place of the fly ash added in Experimental Example 1, the F- concentration was 8 mg/l, the Fe<sup>2+</sup> concentration was 1 mg/l or less, and the Al<sup>3+</sup> was 2 mg/l, thus it was found that if fly ash is added, the F- removal rate can be increased.

It is thought that fluorine components in the desulfurization wastewater can be efficiently removed, as in the foregoing experimental results, because the AI in the fly ash reacts with the F-produce a poorly soluble solid. Furthermore, because soluble salts in the wastewater also react with the CaO in the fly ash, or increase the pH, solids form and precipitate.

# [Effects of the Invention]

With the present invention, pH can be adjusted without using slaked lime and caustic soda, which were heretofore consumed in wastewater treatment systems, and slaked lime, which is used for removing fluorine, is only used supplementally when the pH cannot be adjusted with fly ash alone. Thus, it is possible to effectively utilize the waste fly ash, and

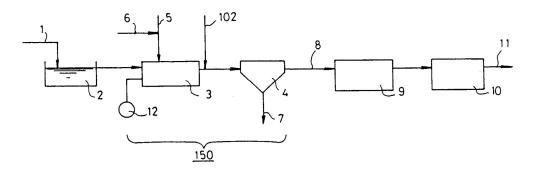
reduce costs associated with additives. Furthermore, fluorine and heavy metals can be simultaneously removed using fly ash, whereby equipment can be downsized by combining the fluorine treatment step and the heavy metal treatment step, which were previously separated, into one step. Further, since solids formed from wastewater and fly ash are neutral, it is not necessary to consider the impact on the surrounding environment.

# 4. Brief Description of the Drawings

FIG. 1 is a schematic view of an example of a desulfurization wastewater treatment device constituting the present invention; and FIG. 2 is a schematic view of a desulfurization wastewater treatment device constituting conventional art.

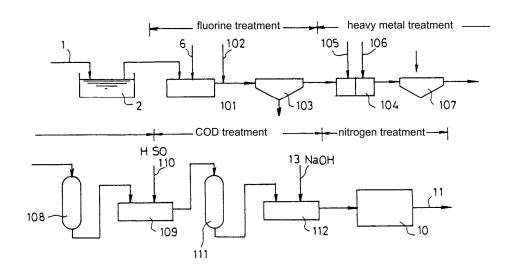
1... desulfurization wastewater, 2... water storage tank, 3... reaction tank, 4... settling tank, 5... fly ash, 6... slaked lime, 7... sludge, 8... supernatant water, 9... COD treatment device, 10... nitrogen compound removal device, 11... treated wastewater, 12... pH meter, 102 ... aggregating agent, 150 ... heavy metal removal device.

Agent: Patent Attorney Takenaga Kawakita



- 1: desulfurization wastewater
- 3: reaction tank
- 4: settling tank
- 5: fly ash
- 6: slaked lime
- 9: COD treatment system
- 10: nitrogen treatment system
- 11: treated wastewater
- 102: aggregating agent

FIG. 2



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Document translated: JP-01-304100-A

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Martin Cross

President, Patent Translations Inc.

4/26/2017

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Bibliographic data: JPH01304100 (A) — 1989-12-07

# APPARATUS FOR TREATING WASTE WATER DESULFURIZED BY WET EXHAUST GAS DESULFURIZATION DEVICE

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Classification: - international: C02F1/52; C02F9/00; (IPC1-7): C02F9/00

- cooperative:

Application number:

JP19880134679 19880601

**Priority number** JP19880134679 19880601

(s):

Also published JP2758607 (B2)

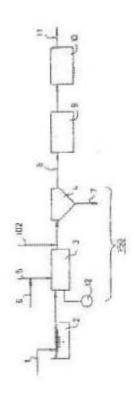
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# Abstract of JPH01304100 (A)

PURPOSE:To permit the removal of heavy metals and fluorine without adding caustic soda and slaked lime or by reducing the added amounts, by providing a heavy metal removal device for adding fly ash to desulfurized wastewater, a COD treatment device therefor and a device for removing nitrogen compounds therefrom.

CONSTITUTION:Desulfurized wastewater 1 stored in a tank 2 is sent to a heavy metal removal device 150 to which fly ash 5 is added, so that the pH value of the wastewater in a reaction tank 3 will become 6-8 when measured by a pH meter 12. A coagulant 102 is added thereto before being sent to a settling tank 4 and the hydroxide and fluorine compounds of precipitated heavy metals are removed as sludges 7 from the bottom of the settling tank 4.; The supernatant water in this settling tank 4 is first sent to a COD treatment device 9 and then after COD removal to a nitrogen compound treatment device 10 for nitrogen component removal. The wastewater 11 thus treated is discharged or can be reused.

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# ⑩ 日本国特許庁(JP)

① 特許出願公開

# ② 公開特許公報(A) 平1-304100

⑤Int. Cl. 4

識別記号 庁内整理番号 ❸公開 平成1年(1989)12月7日

C 02 F 9/00 Z - 7308 - 4D

審査請求 未請求 請求項の数 1 (全4頁)

69発明の名称 湿式排ガス脱硫装置からの脱硫排水処理装置

> 願 昭63-134679 ②1特

22出 願 昭63(1988)6月1日

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> 明 細 書

## 1.発明の名称

湿式排ガス脱硫装置からの脱硫排水処理装置 2. 特許請求の範囲

(1)排ガス中の硫黄酸化物を吸収剤スラリによ り吸収除去する湿式排ガス脱硫装置からの脱硫排 水処理装置において、脱硫排水に石炭燃焼灰(フ ライアッシュ)を添加して同排水中の重金属成分 および/またはフッ素成分を除去する重金属除去 装置と、該装置から排出された処理排水をCOD 処理するCOD処理装置と、このCOD処理され た排水中の窒素化合物を除去する窒素化合物除去 装置とを設けたことを特徴とする湿式排ガス脱硫 装置からの脱硫排水処理装置。

# 3. 発明の詳細な説明

# (産業上の利用分野)

本発明は湿式排ガス脱硫装置からの脱硫排水処 理装置に係り、特に同排水中の重金属成分などを 除去するに好適な湿式排ガス脱硫装置からの脱硫 排水処理装置に関する。

#### 〔従来の技術〕

東京都千代田区大手町2丁目6番2号

一般に、石炭や石油を燃焼する場合、発生する 排ガス中に硫黄酸化物および窒素酸化物等が含ま れており、大気汚染の原因となっている。このた めに、排ガス中のこれらの有害物質を除去するた め、湿式排ガス脱硫装置で硫黄酸化物の処理が行 なわれるが、それに伴って湿式排ガス脱硫装置か ら脱硫排水が排出される。これらの脱硫排水中に は、浮遊物質、重金属、無機イオンおよび有機物 等が含まれており、環境を汚染し種々の弊害をも たらすため、そのまま放流することができない。

石炭焚き火力発電所の湿式排ガス脱硫装置の排 水処理システムの例を第2図に示す。脱硫排水1 は貯水槽2に蓄えられる。次に、反応槽101で 消石灰6を加え、さらに沈澱槽103に送る前に 凝集剤102を加えてフッ素を沈澱分離する。 p H 調整酸化凝集槽 1 0 4 でさらに苛性ソーダ 1 0 5と凝集剤106を加え、沈澱槽107で重金属 を沈澱して除去し、濾過器108を通す。この炉 液は、吸収塔内で生成するジチオン酸(S。〇6

2-) を含んでおり、これはCODの原因となるので除去を必要とする。ジチオン酸の除去は、pH 調整槽109で硫酸110を加えることによりpH調整した後、COD除去塔111を通し中和槽112で苛性ソーダ13を加え中性にする。これらのフッ素、重金属、COD処理により、処理排水11はSSおよびCOD10~15g/ឧ以下、フッ素15ppm以下、油分1ppm以下となって排出基準を満足する。

なお、上記排出水は、若干の窒素化合物を含む。これは、主としてガス中のNOx(ほとんどNOでわずかなNO2を含む)の一部(1~2%程度)が吸収されることによるもので、硝酸態が主であるが、イミドジスルホン酸のように窒素と硫黄を含む化合物もわずかに含まれる。通常、処理排水11中の窒素濃度は500ppm以下であり、窒素処理システム10を動かすことにより、処理排水11の窒素濃度を10ppm以下にすることができる。

一方、石炭焚き火力発電所の電気集塵器で集め

られた石炭灰、すなわちフライアッシュは、一部はセメント、土木材料、肥料、土壌改良材などとして有効に利用されるが、大部分は埋立投棄せざるを得ないのが実態である。埋立投棄する場合は、フライアッシュからの溶出水はアルカリ性であるため、周囲の環境に与える影響を考慮する必要がある。

#### (発明が解決しようとする課題)

上記したように従来技術は、フライアッシュからの溶出水は主にアルカリ性であるため、周囲の 環境に与える影響を考慮する必要があった。また、 脱硫排水中の重金属類およびフッ素を除去するために、苛性ソーダおよび消石灰を添加しており、 この薬品コストによる運転コストの増大、および 薬品貯蔵設備を必要とするなどの問題があった。

本発明の目的は、苛性ソーダおよび消石灰を添加せずに、あるいは添加量を低減し、重金属類およびフッ素を除去することにある。

#### (課題を解決するための手段)

上記した従来技術の問題点は、排ガス中の硫黄

#### 〔実施例〕

第1図は、本発明になる脱硫排水処理装置の実施例を示す。

第1図において、湿式排ガス脱硫装置からの脱硫排水1は貯水槽2に蓄えられる。次にこれは重金属除去装置150に送られる。すなわち、反応槽3に送られ、pHメータ12により反応槽3のpH値が6~8になるようフライアッシュ5が添加される。フライアッシュ5を添加してもpH値が所定値まで高くならない場合は、消石灰6をフ

ライアッシュ 5 に添加する場合もある。沈澱槽 4 に送る前に凝集剤 1 0 2 を加え、沈澱した重金属類の水酸化物やフッ素化合物は、沈澱槽 4 の底部よりスラッジ 7 として抜出される。これらのスラッジ 7 は脱水後、埋立材等に使用できる。沈澱槽 4 の上澄水 8 は C O D 処理装置 9 に送られ、 C O D を除去した後、窒素化合物処理装置 1 0 に送られ、 空素成分が除去される。窒素成分除去かわった処理排水 1 1 は放流されるか、それとも再利用される。

石炭焚き火力発電所からのフライアッシュ5は主成分としてシリカ(SiO2)、アルミナ(AL2O3)および生石灰(CaO)等を含んでいる。生石灰は約1~10%含まれており、水と反応して消石灰(Ca(OH)2)と炭酸カルシウム(CaCO3)になる。フライアッシュ5を排水に添加するとpH値が高くなるのは、生石灰(CaO)が含まれているからである。石炭の種類によっては、フライアッシュ中の生石灰の含有率が低く、排水のpH調整が困難となる場合がある

ので、補助的に消石灰 (Ca (OH) 2) をフライアッシュに添加することができるシステムとなっている。

本発明に基づき、次に述べる実験を行ない、本 発明の効果を確認した。

実験に供した供試脱硫排水の組成は次のとおり である。

p H : 1.2 S S :  $7600 \, \text{mg} / \ell$  C  $\ell$  - :  $3700 \, \text{mg} / \ell$  F - :  $620 \, \text{mg} / \ell$  N a + :  $2700 \, \text{mg} / \ell$  M g  $^{2+}$  :  $615 \, \text{mg} / \ell$  C a  $^{2+}$  :  $306 \, \text{mg} / \ell$  F e  $^{2+}$  :  $132 \, \text{mg} / \ell$ 

A  $\ell^{3+}$ :  $47 \text{ mg} / \ell$ 

#### 実験例1

上記排水1ℓをビーカに採取し、緩やかに電磁 攪拌しながらpHが7.0となるように、同じ発電 所より回収したフライアッシュを添加し、約10 分間攪拌を続けた。その後、攪拌を止め約30分 放置後、ビーカ上部の上澄液をサンプリングして 分析したところ、F-濃度:6 mg/ℓ、Fe²+濃 度:1 mg/ℓ以下、Aℓ³+:2 mg/ℓとなった。

# (発明の効果)

# 4. 図面の簡単な説明

第1図は、本発明になる脱硫排水処理装置の実施例説明図、第2図は、従来技術になる脱硫排水処理装置の説明図である。

#### 比較例1

実施例 1 で加えたフライアッシュの代わりに C a  $(OH)_2$  を用いて以下同様の操作を行なったところ、 $F^-$  濃度: 2 7 mg /  $\ell$  、F e 2 + 濃度: 1 mg /  $\ell$  以下、 A  $\ell$  3 + : 2 mg /  $\ell$  となった。

この結果より、Ca(OH)2のみではF<sup>-</sup>が 液中に残存し、その除去率が悪いことを確認した。 実験例2

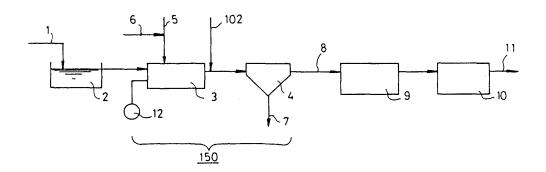
実験例 1 で加えたフライアッシュの代わりに、フライアッシュと消石灰を 1 対 1 の割合で混合した混合物を用いて同様の操作を行なったところ、F - 濃度: 8 mg / ℓ 以下、A ℓ 3+: 2 mg / ℓ となり、フライアッシュを添加するとF - の除去率が髙められるのが確認できた。

上記実験結果のように、脱硫排水中のフッ素成分が効率よく除去できるのは、フライアッシュ中のA&がF-と反応し、難溶性の固形分を生成するためと考えられる。また、排水中の可溶性の塩もフライアッシュ中のCaOと反応し、あるいはpHが高められるため、固形物を生成し沈澱する。

1 … 脱硫排水、 2 … 貯水槽、 3 … 反応槽、 4 … 沈報槽、 5 … フライアッシュ、 6 … 消石灰、 7 … スラッジ、 8 … 上澄水、 9 … C O D 処理装置、 1 0 … 窒素化合物除去装置、 1 1 … 処理排水、 1 2 … p H メータ、 1 0 2 … 凝集剤、 1 5 0 … 重金属除去装置。

代理人 弁理士 川 北 武 長

# 第 1 図



1:脱硫排水

3:反応槽

1:沈殿槽

5:フライアッシュ

6:消石灰

9:COD処理システム

10:窒素処理システム

11: 処理排水

102:凝集剂

# 第 2 図

