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(54) <b>Title of the Invention:</b>	Device for treating desulfurization wastewater from wet flue gas desulfurization device		
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**Specification****1. Title of the Invention**

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 NO<sub>x</sub> 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 ( $\text{Ca}(\text{OH})_2$ ) 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
Cl <sup>-</sup> :	3700 mg/l	F <sup>-</sup> :	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<sup>-</sup> 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  $\text{Ca}(\text{OH})_2$  was used in place of the fly ash added in Example 1, and from that point onward the same operations were performed, the F<sup>-</sup> concentration was 27 mg/l, the Fe<sup>2+</sup> concentration was 1 mg/l or less, and the Al<sup>3+</sup> was 2 mg/l.

From these results, it was found that, with  $\text{Ca}(\text{OH})_2$  alone, the F<sup>-</sup> 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<sup>-</sup> 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<sup>-</sup> 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 Al in the fly ash reacts with the F<sup>-</sup> to 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.

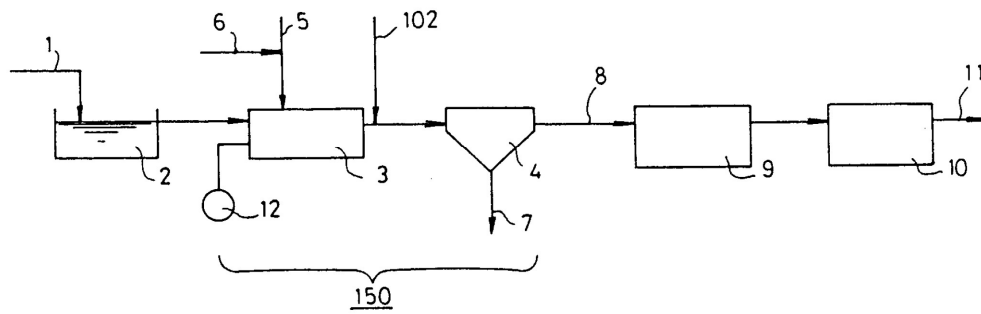
#### 4. Brief Description of the Drawings

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.

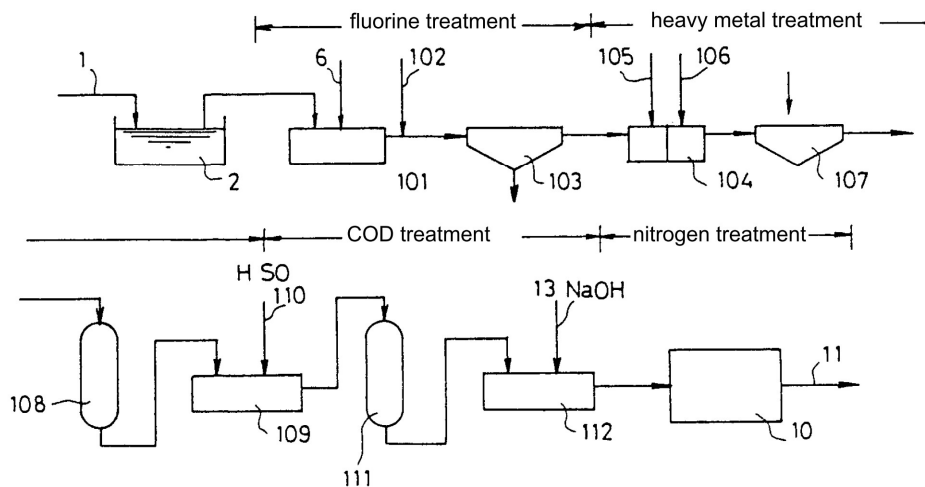
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FIG. 1



- 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



## Certification of Translation

Translator's Declaration: May 16, 2017

I, Martin Cross, hereby declare:

That I possess advanced knowledge of the Japanese and English languages. My qualifications are as follows:

- over 25 years as a Japanese-English translator focusing primarily on patents, and technical and scientific documents;
- co-author of the *Japanese Patent Translator's Handbook*, published by American Translators Association;
- United States district court recognition as an expert in Japanese technical translation for patent litigation; and
- B.A. in English Literature, from York University, courses in Chemistry and Organic Chemistry from Thompson Rivers University.

The attached translation is, to the best of my knowledge and belief, a true and accurate translation from Japanese to English of Japanese Unexamined Patent Application Number JP-01-304100-A. I understand that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. 1001), and may jeopardize the validity of the application or any patent issuing thereon. I declare under penalty of perjury that all statements made herein of my own knowledge are true, and all statements made on information and belief are believed to be true.

Martin Cross

