

Method and system for scrubbing exhaust gases from an engine of a marine vessel

The present invention relates to a method for scrubbing exhaust gases from an engine of a marine vessel, as well as to an installation for applying this method.

Marine vessels whether these are liners or other vessels, use as fuel for their diesel engines, fuel oil. This fuel contains up to 5% by mass of sulfur, most often between 0.5 and 3.5% by mass. During the combustion process in the engines, this sulfur is transformed into sulfur dioxide (SO_2), which is an acid gas.

Marine regulations in effect make it compulsory to limit rejection through the chimney of the vessels to an equivalent of 0.5% by mass of sulfur in the fuel oil powering the engines of the vessels. However the limiting rejection value depends on the navigation area: near coasts or else in harbors, sulfur dioxide emissions should be less than in the opens sea. It should be noted that, even in a harbor, a liner, for example a cruising liner, has to continue operating its engines for meeting on-board electricity needs and therefore, potentially, emits sulfur dioxide.

In order to comply with the aforementioned regulations, it is therefore necessary that marine vessels use means for reducing their sulfur dioxide emissions. Several solutions may be contemplated.

First of all, the sulfur content of the fuel oil used may be reduced, which immediately causes a reduction of sulfur dioxide emissions. However, fuel oil with a very low sulfur content is expensive so that this approach is not economically viable.

It is possible to use a humid scrubbing unit with a neutralization reagent like soda. However, the amounts of soda to be provided are substantial, and since the flow of sulfur dioxide may attain 500 kg/h and per scrubbing unit for very large liners. In addition to the price of soda, its storage has to be provided and its highly caustic nature has to be taken into account with the implied safety risks.

Finally, desulfurization scrubbers with seawater may be contemplated: this technology which uses the natural alkalinity of seawater for neutralizing sulfur dioxide, is a known and under control, especially for energy production plants located on the seaside. The water leaving these scrubbers is acid and requires post-dilution with even more seawater than what is required for simply capturing sulfur dioxide. WO 2011/073503 provides an example of this. This having been said, the application of this technology is a priori not possible on board a vessel which has to navigate in waters with variable salinity and alkalinity. For its part, US 2010/0206171, which discloses a scrubbing method in which the exhaust gases of a marine engine are sent to a desulfurization scrubber with seawater, the

effluents of which are sent for oxidation and dilution to a device supplied with air and sea water, actually proposes controlling both seawater flow rates and the corresponding airflow, without however specifying the specificities of these controls. In every case, on the one hand, provision must be made for pumping significant and variable amounts of water, and this over significant heights, which induces substantial energy consumption for the corresponding pumps. On the other hand, as the waters leaving the scrubber are acid and reducing waters, their discharge into the sea poses a problem of corrosion towards the equipment, as well as a downstream problem of ecotoxicity, because of their large COD (chemical oxygen demand), and a downstream acidification problem because their oxidation continues in the sea, transforming the weak acid, i.e. the captured sulfur dioxide SO_2 or its equivalent H_2SO_3 , into a strong acid, i.e. sulfuric acid.

The object of the present invention is to propose a desulfurization method for gas emissions from marine vessels, which, while retaining acceptable desulfurization performances, consumes less energy and results in less restrictive effluents.

For this purpose, the object of the invention is a method for scrubbing exhaust gases from an engine of a marine vessel, wherein:

- the exhaust gases are sent to a desulfurization scrubber, to which a first flow of seawater is admitted,

- the sulfur dioxide concentration is permanently measured in the gases purified by the scrubber, the flow rate of the first seawater flow being controlled from this measurement of the sulfur dioxide concentration,

- the effluents from the scrubber are connected in an oxidation device, to which an airflow is admitted and to which an iron salt flow is sent directly or via the scrubber,

- the redox potential is permanently measured at the outlet of the oxidation device, the airflow rate and/or the iron salt flow rate being controlled from this measurement of the redox potential,

- the flow leaving the oxidation device is sent to a post-dilution device, which is located at least ten meters lower than the scrubber and to which a second seawater flow is admitted, and

- the pH is permanently measured at the outlet of the post-dilution device, the flow rate of the second seawater flow being controlled from this measurement of the pH.

One of the ideas at the basis of the invention is to minimize the energy required for pumping the first and second seawater flows, by coupling with each other the localization of the post-dilution device much lower than that of the desulfurization scrubber and the control of the flow rates of these first and second seawater flows according to actual needs,

respectively given by the measurement of the sulfur dioxide concentration in the purified gases leaving the scrubber and by the measurement of the pH at the outlet of the post-dilution device. Further the use of an iron salt leads to both reducing the required amount of seawater provided by the first seawater flow, since iron promotes gas-liquid transfer of the sulfur dioxide, by oxidation catalysis, and to reducing the reducing nature of the effluents from the scrubber and therefore the ecotoxic and corrosive nature of the final discharge into the sea.

According to advantageous additional features of the method according to the invention, taken individually or according to all the technically possible combinations:

- the iron concentration in the effluents from the scrubber is maintained between 1 and 10 $\mu\text{moles/L}$;

- the iron salt flow is mixed with the first seawater flow;

- the iron salt is ferric chloride;

- an alkaline agent flow is admitted into the scrubber;

- when the accumulated flow rate of the first and second seawater flows is limited to below the controlled value from the measurement of the sulfur dioxide concentration and from the measurement of the pH, the flow rate of the alkaline agent flow is controlled from the measurement of the sulfur dioxide concentration and from the measurement of the pH; and

- the alkaline agent is magnesia $\text{Mg}(\text{OH})_2$.

The object of the invention is also an installation for scrubbing exhaust gases from an engine of a marine vessel, which installation comprises:

- a desulfurization scrubber, which is adapted for receiving exhaust gases and which is adapted for being supplied with a first seawater flow,

- first measurement means adapted for permanently measuring the sulfur dioxide concentration in the gases purified by the scrubber,

- first control means adapted for controlling the first seawater flow from the measurement provided by the first measurement means,

- an oxidation device, which is adapted for connecting the effluents of the scrubber, which is adapted for being supplied with an airflow and which is adapted for receiving, either directly or via the scrubber, an iron salt flow,

- second measurement means adapted for permanently measuring the redox potential at the outlet of the oxidation device,

- second control means adapted for controlling the airflow rate and/or the iron salt flow rate from the measurement provided by the second measurement means,

- a post-dilution device, which is adapted for receiving the flow leaving the oxidation device, which is located at least ten meters lower than the scrubber and which is adapted for being supplied with a second seawater flow,

- third measurement means adapted for permanently measuring the pH at the outlet
5 of the post-dilution device, and

- third control means adapted for controlling the flow rate of the second seawater flow from the measurement provided by the third measurement means.

The installation according to the invention gives the possibility of applying the method as defined above and is designed so as to be loaded onboard a marine vessel for a
10 efficiently and economically desulfurizing the gas emissions.

According to advantageous additional features of this installation:

- the oxidation device is integrated at the bottom of the desulfurization scrubber; and
- the insulation further comprises a means for admitting an alkaline agent to the desulfurization scrubber.

15 The invention will be better understood upon reading the description which follows, only given as an example and made with reference to the drawings wherein:

- Fig. 1 is a diagram of an installation allowing application of a method according to the invention; and

- Fig. 2 is a diagram of the oxidation kinetics of the sulfur in solution versus the iron
20 concentration.

In Fig. 1, an engine, for example a diesel engine, of a ship emits exhaust gases 1 which are sent into a desulfurization scrubber 100, i.e. a scrubber designed for capturing sulfur dioxide (SO_2) contained in the exhaust gases 1. The exhaust gases 1 are generally available at a temperature comprised between 220 and 350°C, this temperature depending
25 on boilers and on economizers which may recover heat upstream from the scrubber 100.

The scrubber 100 uses seawater for capturing sulfur dioxide, so that a substantial seawater flow has to be sprayed thereon. The scrubber 100 also has a quenching function, in the sense that it cools the gases down to the equilibrium temperature with water, this equilibrium temperature generally being comprised between 20 and 40°C, its value varying
30 according to the temperature of the sea water used and according to the temperature of the gases, in particular.

The portion 101 of the scrubber 100, active for capturing sulfur dioxide, uses a technology known *per se*: this active portion 101 comprises, *inter alia*, packing or plates and/or sprayers. An optionally diluted seawater flow 2' is admitted to the active portion 101 of
35 the scrubber 100. As the alkalinity of seawater is low, typically with a value of 1,000 to 2,500

micro-equivalents of alkalinity per liter, depending on the geographic localization, this forces the use of a substantial flow rate for the seawater flow 2'. As an order of magnitude, for a flow rate with a value of 120 000 Nm³/h of exhaust gases 1 containing 300 kg/h of SO₂, the flow rate for the seawater flow 2' is of the order of 1,000 m³/h.

5 For implementation reasons specific to marine vessels, the scrubber 100 is not placed here in the hold, so that the seawater flow 2' has to be pumped with a pump 200 which has to raise seawater over several tens of meters and through pipes, which thus generates a substantial pressure drop and entails high energy costs. As explained subsequently, one of the pursued goals of the invention is to minimize the flow rate of the seawater flow 2', while
10 retaining acceptable desulfurization performances.

The effluents of the scrubber 100, i.e. the waters having captured sulfur dioxide upon passing in the active portion 101 of the scrubber after having been distributed to the scrubber, are very acid, with a pH normally comprised between 2 and 4, most often comprised between 2 and 3, and they are strongly reducing agents.

15 According to one of the features of the invention, the effluents of the scrubber 100 are collected in an oxidation device 300 designed for promoting, in the presence of air, oxidation of the sulfur from state (+4) to state (+6), in other words designed for promoting in the presence of oxygen, the transition from sulfites to sulfates. For this purpose, the oxidation device 300 is supplied with an airflow 3 which is directly admitted, notably injected into the
20 collected effluents of the scrubber: the corresponding means of the oxidation device 300 are known per se and for example comprise distribution ramps and/or injectors.

In the relevant exemplary embodiment in Fig. 1, the oxidation device 300 is integrated at the bottom of the scrubber 100, but as a functionally similar alternative not shown, this oxidation device may be moved away or even separated from the scrubber 100, as an
25 ancillary container.

Regardless of its embodiment, it is understood that the oxidation device 300 gives the possibility of correcting the reducing nature of the effluents of the scrubber 100.

According to another feature of the invention, an iron salt, preferably ferric chloride flow 6 is admitted into the oxidation device 300, so as to accelerate and facilitate oxidation of
30 the effluents of the scrubber 100. Indeed, it is known that iron, as well as moreover other metals at concentrations comprised between 1 and 10 µmoles/L, has a considerable effect on the oxidation kinetics of sulfites. As example, Fig. 2, established from research work results dating back to 1977 (S. Fuzzi), shows the significant effect of iron on the oxidation of sulfur in solution, the axis of the abscissas of Fig. 2 corresponding to the iron concentration
35 in solution, while the axis of the ordinates corresponds to the constant K of second order

kinetics of oxidation of sulfur in solution: the effect depends on the pH, as illustrated by both curves of Fig. 2 which correspond to a respective pH values of 3 and 4.

In the exemplary embodiments considered in Fig. 1, the iron salt flow 6 is mixed with the seawater flow 2'. This being the case, it is understood that the exact location of injection of the iron salt flow has no importance from the moment that the iron salt is again found in one way or the other in the effluents collected in the oxidation device 300.

According to a feature of the invention, the air flow rate 3 and/or the flow rate of the iron salt 6 are if necessary controlled by *ad hoc* means, from the measurement of the redox potential, currently called oxidation-reduction potential (ORP), of the effluents oxidized by the oxidation device 300: for this purpose, a probe 400 is use which permanently measures this redox potential. In practice, the probe 400 is placed at the outlet of the oxidation device 300, it being understood that this « output » displacement corresponds both to the arrangement of the probe 400 at a conduit for channeling the flow 4 coming out on the outside of the oxidation device 300, and to the use of this probe in an area of the oxidation device, in which the oxidation of the effluents is substantially completed.

Advantageously, for the reasons mentioned above, the flow rate of the iron salt flow 6 is controlled so that the iron concentration in the effluents collected in the oxidation device 300 is maintained between 1 and 10 $\mu\text{moles/L}$.

By oxidation of the effluents of the scrubber, achieved by the oxidation device 300 supplied with the airflow 3 and increased with the iron salt flow 6, the flow 4 leaving the device 300 is both less noxious for the environment and less aggressive for the equipment, because it contains oxidized sulfates instead of non-oxidized sulfites.

Moreover, according to another feature of the invention, the acidity of the flow 4 leaving the oxidation device is treated as so as to be able to be discharged into the sea. To do this, post-dilution of this flow 4 is achieved with a seawater flow 2'', the alkalinity provided by the latter allows the pH to be raised, notably for observing the pH constraints in the wake of the vessel. According to the invention, in order to minimize the total required energy, this post-dilution is achieved in an *ad hoc* device 500, which is for example a dilution container or a static mixer and which receives the seawater flow 2'', distinct from the seawater flow 2' and driven by a specific pump 600. At the outlet of the post-dilution device 500 a final rejection flow 5 is formed, discharged out of the ships, by being discarded into the sea.

A pH-meter 700 is used for appreciating the effect on the pH by the post-dilution device 500, so that the measurement which it permanently provides is used if necessary for controlling with *ad hoc* means, the flow rate of the seawater flow 2''. In practice, the pH-meter 700 is placed at the output of the post-dilution device 500, it being understood that this

« output » placement also corresponds to the layout of the pH-meter 700 at a conduit channeling the discharge flow 5 out of the post-dilution device 500, and to the use of this pH-meter in an area of the post-dilution device, in which the mixture of the flows 2'' and 4 is substantially homogenized.

5 It should be well understood that, by not using any alkaline neutralizing agent other than seawater, the flow rate of the total seawater flow 2, corresponding to the accumulation of the seawater flows 2' and 2'', is given for observing the constraints as regards pH in the final discharge flow 5. According to an important feature of the invention, the post-dilution device 500 is located at least ten meters below the scrubber 100. More specifically, the distance of at least 10 meters between both of these pieces of equipment should be considered between the bottom of the post-dilution device 500 and the bottom of the scrubber 100. By localizing the post-dilution device 500 well below the scrubber 100, significant savings are made for the energy required for operating the pumps 200 and 600.

10 Further, the scrubbing yield, defined by the equation $(1 - c_s/c_i)$ wherein c_s and c_i are the sulfur dioxide concentrations in the flow of purified gases 7 and in the exhaust gases 1 respectively, is directly impacted by the liquid/gas ratio of the mass flow rates of the seawater flow 2' and of the airflow 3, this yield being also impacted by other factors such as the pH and the temperature. According to one of the features of the invention, a sulfur dioxide analyzer 800, located at the outlet of the scrubber 100, and apparently it measures the sulfur dioxide concentration in the purified gases 7, this measurement being used for controlling, if necessary by *ad hoc* means, the flow rate of the seawater flow 2'. Thus, it is understood that permanently, the share of the seawater flow 2', over the total seawater flow 2 is minimized, while the remainder of the total flow 2, i.e. the seawater flow 2'', is sent by the pump 600 of the post-dilution device 500, much lower in elevation than the scrubber 100, and therefore with less energy.

25 Moreover, it should be noted that when the iron salt flow 6 is sent to the scrubber 100, the introduction of iron « draws » sulfur dioxide towards the liquid, since sulfur dioxide has only limited solubility in water, unlike sulfuric acid produced by the oxidation, which is practically extremely soluble. It is understood that the presence of the iron salt brought by the flow 6 therefore allows further decrease in the seawater flow rate 2'.

30 The invention thus ensures the following advantages:

- control of the flow rates of the seawater flows 2 and 2'' according to actual needs, which are determined by measurements provided by the analyzer 800 and the pH-meter 700, a control coupled with the localization of the post-dilution device 500 at a much lower

elevation than the scrubber 100, retains to a strict minimum, the total energy was spent for pumping the seawater flows 2' and 2'';

- by the use of iron, which accelerates oxidation and that reduces the reducing nature of the effluents of the scrubber 100 and therefore of the final discharge 5, the ecotoxic nature towards the environment and the corrosive nature towards the equipment are decreased; and

- the use of iron also improves the gas-liquid transfer of sulfur dioxide in the effluents of the scrubber 100, by oxidation catalysis, and further decreases the required flow rate for the seawater flow 2'.

Optionally, the desulfurization installation is advantageously completed with a means for introducing an alkaline agent into the supply of the scrubber 100, as indicated by a flow 8 in dotted lines in Fig. 1. This alkaline agent is for example magnesia $Mg(OH)_2$ or soda $NaOH$. When the ship is in the open sea or more generally when no limitation affects the flow rate values of the seawater flows 2' and 2'', controlled from the measurements by the analyzer 800 and by the pH-meter 700, the alkalinity brought by the alkaline agent 8 is marginal relatively to that brought by the seawater flow 2': in other words, in these cases, the invention corresponds to desulfurization essentially or even exclusively with seawater. This being the case, in certain situations, for example when the ship is in a harbor or, more generally, when the accumulated flow rate of the seawater flows 2' and 2'' is limited to below the controlled flow rate value from the measurements of the analyzer 800 and from the neutral pH 700, the alkalinity brought by the alkaline agent flow 8 becomes predominant relatively to the alkalinity brought by the seawater flow 2', the latter may be marginal: in those cases, the flow rate of the alkaline agent flow 8 is controlled, if necessary with *ad hoc* means, from the measurements provided both by the analyzer 800 and the pH-meter 700.

In practice, it is understood that the exact location of the point for injecting the alkaline agent flow 8 is unimportant from the moment that the alkaline agent is again found in one way or the other, in the scrubbing liquid used in the scrubber 100: thus, the alkaline agent flow 8 may be directly introduced into the scrubber 100 or into the supply circuits of the latter.

It will be noted that the various control means mentioned up to now are not illustrated in Fig. 1 and for example comprise a regulator, a calculator, an automated system and/or a computer control unit, etc.

CLAIMS

1. A method for scrubbing exhaust gases from an engine of a marine vessel, wherein:

- the exhaust gases (1) are sent to a desulfurization scrubber (100), to which a first seawater flow (2') is admitted,
- the sulfur dioxide concentration is permanently measured in the gases (7) purified by the scrubber (100), the flow rate of the first seawater flow (2') being controlled from this measurement of the sulfur dioxide concentration,
- the effluents of the scrubber (100) are collected in an oxidation device (300), to which an airflow (3) is admitted and to which an iron salt flow (6) is directly admitted or via the scrubber (100),
- the redox potential is permanently measured at the outlet of the oxidation device (300), at least one of the airflow rate (3) and the flow rate of the iron salt flow (6) being controlled from this measurement of the redox potential,
- the flow (4) leaving the oxidation device (300) is sent to a post-dilution device (500), which is located at least ten meters lower than the scrubber (100) and to which a second seawater flow (2'') is admitted, and
- the pH is permanently measured at the outlet of the post-dilution device (500), the flow rate of the second seawater flow (2'') being controlled from this measurement of the pH.

2. The method according to claim 1, wherein the iron concentration in the effluents of the scrubber (100) is maintained between 1 and 10 $\mu\text{moles/L}$.

3. The method according to one of claims 1 or 2, wherein the iron salt flow (6) is mixed with the first seawater flow (2').

4. The method according to one of claims 1 or 2, wherein the iron salt is ferric chloride.

5. The method according to claim 1, wherein an alkaline agent flow (8) is admitted to the scrubber (100).

6. The method according to claim 5, wherein, when the accumulated flow rate of the first and second seawater flows (2', 2'') is limited to below the controlled value from the measurement of the sulfur dioxide concentration and from the measurement of the pH, the flow rate of the alkaline agent flow (8) is controlled from the measurement of the sulfur dioxide concentration and from the measurement of the pH.

7. The method according to one of claims 5 or 6, wherein the alkaline agent is a magnesia $\text{Mg}(\text{OH})_2$.

8. An installation for scrubbing exhaust gases from an engine of a marine vessel, which installation comprises:

- a desulfurization scrubber (100), which is adapted for receiving the exhaust gases (1) and which is adapted for being supplied with a first seawater flow (2'),
- first measurement means (800) adapted for permanently measuring the sulfur dioxide concentration in the gases (7) purified by the scrubber (100),
- first control means adapted for controlling the flow rate of the first seawater flow (2') from the measurement provided by the first measurement means,
- an oxidation device (300), which is adapted for connecting the effluents of the scrubber (100), which is adapted for being supplied with an airflow (3) and which is adapted for directly receiving or via the scrubber (100), an iron salt flow (6),
- second measurement means (400) adapted for permanently measuring the redox potential at the outlet of the oxidation device (300),
- second control means adapted for controlling at least one of the airflow rate (3) and the flow rate of the iron salt flow (6) from the measurement provided by the second measurement means,
- a post-dilution device (500), which is adapted for receiving the flow (4) leaving the oxidation device (300), which is located at least ten meters lower than the scrubber (100) and which is adapted for being supplied with a second seawater flow (2''),
- third measurement means (700) adapted for permanently measuring the pH at the outlet of the post-dilution device (500), and
- third control means adapted for controlling the flow rate of the second seawater flow (2'') from the measurement provided by the third measurement means.

9. The installation according to claim 8, wherein the oxidation device (3) is integrated to the bottom of the desulfurization scrubber (100).

10. The installation according to one of claims 8 or 9, which installation further comprises a means (8) for admitting an alkaline agent to the desulfurization scrubber (100).