

# Exhaust Gas Scrubber Installed Onboard MV Ficaria Seaways

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Exhaust Gas Scrubber Installed Onboard MV Ficaria Seaways

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# Table of Contents

INTRODUCTION	5
SAMMENFATNING OG KONKLUSIONER	7
SUMMARY AND CONCLUSIONS	9
1 LEGISLATION AND APPROVAL	11
2 INSTALLATION	13
<ul> <li>2.1 SEAWATER MODE (SW)</li> <li>2.2 FRESHWATER MODE (FW)</li> <li>2.3 ENERGY CONSUMPTION</li> <li>2.4 DATA ACQUISITION</li> </ul>	14 15 16 17
3 GAS MEASUREMENTS	18
<ul> <li>3.1 Measuring principle</li> <li>3.2 Calculation of fuel sulphur equivalent</li> <li>3.3 SO<sub>2</sub> removal</li> <li>3.4 PM removal</li> <li>3.5 NO<sub>x</sub> removal</li> </ul>	Т 18 Т 18 18 19 20
4 DISCHARGE WATER ANALYSIS	21
<ul> <li>4.1 SEAWATER MODE <ul> <li>4.1.1 pH</li> <li>4.1.2 Turbidity</li> <li>4.1.3 Polycyclic Aromatic Hydrocarbons (PAH<sub>phe</sub>)</li> <li>4.1.4 Suspended Solids</li> <li>4.1.5 Oil in Water</li> <li>4.1.6 Nitrate</li> <li>4.1.7 Heavy metals</li> </ul> </li> <li>4.2 FRESH WATER MODE <ul> <li>4.2.1 pH</li> <li>4.2.2 Turbidity</li> <li>4.2.3 Polycyclic Aromatic Hydrocarbons (PAH<sub>phe</sub>)</li> <li>4.2.4 Heavy metals</li> <li>4.2.5 Nitrite and nitrate</li> </ul> </li> </ul>	21 21 22 23 24 24 24 24 25 25 25 25 25 26 26 26
5 DISCUSSION	27
6 ABBREVIATIONS	28
7 REFERENCES	30

# Introduction

An exhaust gas scrubber has been installed on-board the DFDS vessel Ficaria Seaways (Tor Ficaria until July 22, 2011) as a retrofit along with an elongation of the ship at yard (MWB Moterenwerken Bremerhaven AG) in July 2009. Only main items like the scrubber and water pump were installed at yard, while all piping and electrical wiring were made subsequently with the ship in operation. The scrubber is the largest scrubber in the world installed on a marine vessel and the first installed after a 2-stroke main engine (21060 kW MAN B&W engine, 9L60MC-C8-TI). Exhaust gas scrubbers have also been installed on marine vessels by Marine Exhaust Solutions, Wärtsila, Clean Marine, and Hamworthy-Krystallon after 4-stroke engines.

Ficaria Seaways is a ro-ro vessel in route between Goteborg - Immingham (1 trip per week), Immingham – Goteborg (2 trips per week), Goteborg – Brevik (1 trip per week), and Brevik – Immingham (1 trip per week). The scrubber has been in operation since 1<sup>st</sup> of June 2010.

The project began in 2008 with land based tests where a scrubber was installed after a smaller 1000 kW 4-stroke MAN engine in Holeby - DK. These tests showed SO<sub>2</sub> removal efficiencies at >98 % and particle removal efficiencies up to 80 % from the exhaust gas. Based on these tests and promising results, a scrubber for Ficaria Seaways was designed early 2008 and installed during 2009. The project is a co-operation between Alfa Laval Aalborg (Aalborg Industries until May 13, 2011), MAN Diesel & Turbo, and Alfa Laval and has been co-financed by the Danish Environmental Agency under a program for testing and promoting new environmental technologies.

# Sammenfatning og konklusioner

Hovedproblemet ved emissioner af svovldioxid  $(SO_2)$  er dannelsen af syreregn og ultrafine partikler (PM) i atmosfæren, der delvist bæres ind over land og kan trænge ned i lungerne på mennesker. Størstedelen af de ultrafine partikler forårsages af  $SO_2$ , der oxideres to  $SO_3$  og danner sekundære aerosoler i atmosfæren. Ved hjælp af en skrubber kan  $SO_2$  i udstødningsgassen i stedet neutraliseres til vandopløst sulfat og afledes til havet, der allerede indeholder langt større mængder sulfat af naturlig forekomst.

En scrubber til rensning af udstødningsgas for  $SO_2$  er blevet installeret efter en MAN 21 MW 2-takts motor om bord på DFDS skibet Ficaria Seaways. Scrubberen blev installeret i 2009/2010 og har været i drift i 5630 timer (Juni 2012). Enkelte skrubbere er allerede i drift efter mindre 4-takts motorer på andre skibe. Disse skrubbere renser udstødningsgassen med havvand (SW) eller med ferskvand (FW), men kan ikke som denne skifte mellem SW og FW drift. Denne scrubber blev designet så den kan skifte mellem SW og FW for at opnå mere erfaring med begge driftsformer, og for at sammenligne fordele og ulemper direkte.

Hovedkomponenterne er et gasabsorptionstårn samt et system for tilførsel, cirkulation og afledning af SW eller FW. I SW drift føres vandet en gang igennem skrubberen og afledes direkte til havet. Fordelen ved SW drift er, at der ikke forbruges kemikalier ombord på skibet idet havets naturlige indhold af bikarbonat benyttes til at neutralisere den absorberede SO<sub>2</sub>. I FW drift cirkuleres det samme vand tilbage til skrubberen, og skal kontinuerligt tilsættes natriumhydroxid (NaOH) for at neutralisere den absorberede SO<sub>2</sub>. Fordelen ved FW drift er, at mængden af afledningsvand kun er ca. 1:250 i forhold til SW drift, hvorfor det i FW drift er muligt at implementere en effektiv rensning af afledningsvandet.

De opnåede resultater viser i forlængelse af tidligere gennemførte forsøg på land, at det er muligt at reducere  $SO_2$  emissionen til under 19 ppm. Dette svarer til under 0,10 % svovl i brændstoffet, hvorfor det er muligt at overholde IMO's strengeste svovlkrav, der vil komme til at gælde fra 1. januar 2015.

I skrubberen opfanges der ca. 0,15 kg/MWh sodpartikler i vandet hvilket svarer til 0,8 ‰ af brændstofforbruget. I FW drift vil sodpartiklerne efterfølgende blive separeret fra i en centrifuge og opsamlet i form af en pumpbar slam indeholdende ca. 80-90 % vand. Denne relativt beskedne mængde slam afleveres i havn. Sodpartiklerne består overvejende af uforbrændt kulstof, men indeholder også tungmetaller – særligt vanadium og nikkel samt mindre mængder poly-aromatisk-hydrokarbon (PAH).

Som det fremgår af nedenstående tabel, overholder også afledningsvandet fra skrubberen i både SW og FW drift IMO's guidelines for udstødsskrubbere<sup>2,3</sup>. Disse guidelines for skrubbere er under stadig revision af MEPC/BLG under hensyntagen til virkelige data / erfaringer. Der henvises i den forbindelse til resultaterne og erfaringerne i denne rapport og særligt til afsnit 4.1.3 vedrørende kontinuerlig måling af PAH<sub>abe</sub>.

	рН	Turbiditet ift. indløbsvand [FNU]	PAH <sub>phe</sub>	Nitrat [% fjernelse fra udstødsgassen]
Havvand (SW)	3 to 6 <sup>ª</sup>	< 5	< 1	0,2
Ferskvand (FW)	> 6,5	< 25	< 2	< 1
Max i henhold til MEPC.184(57) (kun i havn)	> 6,5	< 25	< 50	< 12

pH-værdien kan øges ved at fortynde med havvand indenfor eller udenfor skibet. Normaliseret for et vandforbrug på 45 m<sup>3</sup> per MWh motorydelse. a)

b)

Brændstofforbruget vil øges med ca. 1,4 % på grund af energiforbruget forbundet med at pumpe vand i systemet og på grund af et svagt øget modtryk på udstødningsgassen fra motoren. I FW drift vil energiforbruget øges yderligere, på grund af forbruget af natriumhydroxid, der skal produceres på land. Alt i alt svarer energibruget i ferskvandsdrift til ca. 3.4 % af energien i brændstoffet. Alternativet - at producere lavsvovlholdigt destillatolie – vil forårsage op til 15 % ekstra  $CO_2$  emission pga. et øget energiforbrug på olieraffinaderierne.

# Summary and conclusions

The main environmental concern regarding emissions of sulphur dioxide  $(SO_2)$  is formation of acid rain and ultrafine particles in the atmosphere, which are partly born to land and which can penetrate into human lungs. Much of the ultrafine particles are caused by  $SO_2$ , which oxidizes to  $SO_3$  and forms secondary aerosols in the atmosphere. By aid of a scrubber, the  $SO_2$  can instead be neutralized to water soluble sulphate and discharged to the sea, which already contains much larger quantities of sulphate of natural origin.

An exhaust gas scrubber able to operate in both a seawater (SW) and a fresh water (FW) mode has been installed after a MAN 21 MW 2-stroke engine on-board the DFDS vessel Ficaria Seaways. The scrubber was installed in 2009/2010 and has been in operation for 5630 hours (June 2012). Scrubbers are already in operation after smaller 4-stroke engines on other vessels but these systems cannot switch between SW and FW mode. This scrubber was designed as a so-called hybrid scrubber in order to get more experiences with FW and SW and to compare advantages and disadvantages of the two modes directly.

The main components are a gas absorption tower and a system for supply, circulation and discharge of SW or FW. In SW mode, the water only passes the scrubber one time and is then discharged to the sea. The main advantage of SW operation is that no chemicals are consumed on-board the ship because the natural content of bi-carbonate in the SW is utilized for neutralization of the absorbed SO<sub>2</sub>. In FW mode, the same water is circulated back to scrubber and it is necessary to continuously add sodium hydroxide (NaOH) for neutralization of the absorbed SO<sub>2</sub>. In FW mode, the amount of discharge water is however only 1:250 of that in SW mode whereby it is possible to implement an effective discharge water cleaning unit.

The obtained results show in continuation of previous tests on land, that it is possible to reduce the  $SO_2$  level to under 19 ppm in the exhaust gas. This corresponds to below 0.10 % sulfur in the fuel whereby it is possible to comply with IMO's most strict sulphur requirement, which will prevail from January 2015.

Approximately 0.15 kg/MWh of soot particles are collected by the water in the scrubber. This corresponds to 0.8 ‰ of the fuel consumption. In FW mode, the soot particles will subsequently be separated out in a centrifuge and collected as a pumpable sludge containing approximately 80-90 % water. This relative small amount of sludge is delivered to adequate facilities in port. The soot particles mainly consist of unburned carbon but also heavy metals – especially vanadium and nickel as well as smaller amounts of Poly Aromatic Hydrocarbon (PAH<sub>phe</sub>).

As seen from the table below, also the discharge water is in compliance with IMO's guidelines for exhaust gas scrubbers<sup>2.3</sup>. This is the case both in SW and FW mode. These guidelines are still subject to revision by MEPC/BLG under consideration of real measurements and experiences. In this respect, it is

recommended to pay attention to this report and especially to section 4.1.3 regarding continuous measurement of  $PAH_{obs}$ .

	pH		PAH	Nitrate
		inlet water		[% removal from
		[FNU]	[ppb]⁵	the exhaust gas]
SW mode	3 to $6^{a}$	< 5	< 1	0.2
FW mode	> 6.5	< 25	< 2	< 1
MEPC.184(57)	> 6.5	< 25	< 50	< 12 %
(only in				
harbour)				

The discharge water analysis can be summarized as follows:

a) The pH value can be increased by dilution with seawater inside or outside the ship.

b) Normalized for a water flow on 45 m<sup>3</sup> per MWh of engine power.

The fuel consumption will increase by approximately 1.4 % due to power required for pumping the water (1 % at MCR) and due to a slightly increased back pressure on the exhaust gas from the engine (app. 0.4 %). In FW mode, the energy consumption will increase further due to the consumption of sodium hydroxide that must be produced at land. In total, the energy consumption in FW mode corresponds to 3.4 % of the energy in the fuel oil. This must be compared to the alternative of using low sulphur distillate oil, which can cost up to 15 % additional  $CO_2$  due to an increased energy consumption on oil refineries at land.

# 1 Legislation and approval

IMO's 1997 protocol to amend MARPOL 73/78 added Annex VI -Regulations for the Prevention of Air Pollution from Ships. This entered into force on 19 May 2005. Regulation 14 included a 1.5 % limit on the sulphur content of fuel to be used in Emission Control Areas. Alternatively the use of an approved exhaust gas cleaning system to reduce the total emissions from the ship to an equivalent level was permitted<sup>1</sup>.

Figure 1 below illustrates the maximum HFO sulphur contents, both globally and in ECA-areas where the limits are significant lower according to the IMO criteria. The global decrease from 3.50 % to 0.50% in 2020 is subject to a 2018 review where it is possible, depending on the situation, that the enforcement of the 0.50% limit can be delayed until 2025.



Figure 1: Maximum fuel sulphur contents according to MARPOL ANNEX VI.

As practical experience has grown, the Guidelines for Exhaust Gas Cleaning Systems have been reviewed with a particular focus on "washwater" emissions. This enabled an updated version to be adopted in 2008, IMO Resolution 170(57)<sup>2</sup>, which contained extensive revisions to improve the structure and logic of the document and washwater emissions criteria. It was agreed that the washwater criteria "should be revised in the future as more data becomes available on the contents of the discharge and its effects, taking into account any advice given by GESAMP", The Joint Group of Experts on Scientific Aspects of Marine Environmental Protection - an advisory body to the United Nations. It was also agreed later in 2008 that 170(57) should remain valid until the revised MARPOL Annex VI entered into force in July 2010. In 2009, a third iteration of the Guidelines for Exhaust Gas Cleaning Systems, IMO Resolution 184(59)<sup>3</sup>, was adopted and this latest version replaced 170(57) in July 2010.<sup>1</sup>

Exhaust Gas Scrubbers are also allowed through directive 1999/32/EC to be used to achieve emissions that are equivalent to the sulphur-in-fuel limits either during a trial approved by EU member states or if the equipment has been properly approved, "taking into account guidelines to be developed by IMO."

The scrubber system on-board Ficaria Seaways has been approved according to MEPC.170 (57) for an 18 month test period starting 1<sup>st</sup> March 2010 by the Danish Environmental Protection Agency. The project has further been discussed with Swedish and British authorities as well as Norway, EU and IMO have been informed about the tests. During the test period, real data and experiences have been obtained for permanent approval of the system, as well as for revision of the wash water discharge criteria as mentioned in IMO Resolution MEPC.170 (57). The scrubber is now also approved as a permanent installation by Lloyds Register for Shipping and the Danish Maritime Authorities according to MEPC.170(57).

# 2 Installation

A picture of the scrubber during installation at yard is shown in Figure 2. The diameter of the absorption tower is 4.6 meters and the height of the absorption tower is 10 meters. The scrubber is made in high grade stainless steel (seawater resistant) and has a weight of 32 tonne (incl. water) in operation. The system is designed to treat up to 192,000 kg/h of exhaust gas from the 21 MW MAN engine. In comparison, this main engine (9L60MC-C8-TI) is approximately 11 meter long, 6 meter broad, 14 meters high and 510 tonne in weight. In addition to the scrubber itself, approximately 200 meters of piping has been installed in order to transport water to and from the scrubber. This piping varies between 300 and 500 mm in diameter.

The scrubber on Ficaria Seaways has been designed to operate in two different modes, seawater mode (SW) and freshwater mode (FW). Each of these modes has its own unique way of operating and removing  $SO_x$  from the exhaust gas as will be explained below.



Figure 2: Scrubber during installation at Moterenwerken Bremerhaven in Germany July 2009. See Figure 3 for more detailed flowsheet.

### 2.1 Seawater mode (SW)

While operating in SW mode, the scrubber uses the natural alkalinity of seawater to absorb and bind the  $SO_x$  from the exhaust gas. The alkalinity of seawater varies, depending on geographic location, however at most locations it is appropriate to use a value of approximately 2.2 mmol/L<sup>4</sup>.

In Figure 3, the scrubber operating in SW mode is sketched. The engine exhaust gas from the turbo charger is cooled to approximately 208°C in an exhaust boiler (Alfa Laval Aalborg AQ2, not shown) and passes a silencer (not shown) prior to the scrubber. A main pump feeds water into the scrubber consisting of a jet/venturi, an absorber, and a demister. The main part of the water enters the absorber at low pressure where it is distributed above high surface filling elements.

After passing through the scrubber, the discharge water is let straight back into the ocean. Because of this direct discharge, this is called an 'open loop.'



2.2 Freshwater mode (FW)

While operating in FW mode, the scrubber recycles freshwater in which sodium hydroxide (NaOH) is continuously added in order to balance pH at a slightly alkaline value.

As sketched in Figure 4, the water is stored in a circulation tank and is circulated by aid of a pump through a plate heat exchanger to the scrubber and back to the tank. NaOH can be added either before or after the circulation tank as shown.

The main feature of the FW mode is the ability to circulate the water for more than 6 hours with maximum load on the engine (MCR) and without the need of discharging any water to the sea. The limiting factor for how long the system can operate in completely closed loop in FW mode is mainly the volume of water in the tank, which at some point will be saturated with sodium sulphate. Before reaching this limit, the water must be cleaned for soot particles (but not sodium sulphate) and then discharged. FW mode is also called a 'closed loop' because of the scrubber's ability to circulate the same water without discharge.



Figure 4: Flow sheet FW-mode.

A main drawback of the FW mode is the consumption of sodium hydroxide (NaOH). In this work, it has been found necessary to add approximately 1.75 mole of NaOH per mole of sulphur in the fuel oil. NaOH can be supplied as solid flakes but is usually supplied as a solution in water where the most common concentrations are 27 % or 45 % (w/w). To reduce space

requirements, a 45 % solution was chosen. This will solidify below approximately 8°C, so a heated cabinet was build. This cabinet can store 5 IBC 1000L pallet tanks. The consumption and costs for the NaOH is shown in Figure 5.



Figure 5: Consumption of sodium hydroxide (NaOH) per ton of heavy fuel oil as a function of the fuel oil sulphur content. Blue line is for a theoretical 100 % solution, red and green lines are for the 45 % solution applied on the ship. Purple line is the actual costs incl. transport and delivery of the pallet tanks on-board the ship as well as return of empty pallet tanks (Jan 24, 2011 prices).

### 2.3 Energy consumption

A 180 kW pump has been installed to supply water to the scrubber. At full engine load, this corresponds to max 1 % of the engine power. The scrubber is causing an additional back pressure of up to 30 mbar, which will also cause some additional energy consumption on the main engine. MAN Diesel & Turbo measured the performance of the engine with and without scrubber (by opening/ closing an exhaust bypass valve before the scrubber under constant engine load). The additional energy consumption associated with the scrubber back pressure is within the uncertainties of the engine performance measurements – this is difficult to measure but estimated to 0.4 % by MAN Diesel & Turbo.

In FW mode, energy for producing NaOH must also be taken into account. NaOH can be produced by several methods; most common is Diaphragm Cell Electrolysis, which requires 5000 kWh/ton<sup>5</sup>. This corresponds to a loss on 2.1 % of the energy in the HFO<sup>a</sup>.

Energy required for producing NaOH<sup>5</sup> Energy in HFO HFO sulphur content

5000 kWh/ton = 18000 kJ/kg 41000 kJ/kg HFO 2.2 % (w/w) Using distillate oil (less than 0.1 % sulphur) instead of scrubbers will also cost additional energy because of the oil refinery process in which the fuel has to be heated, pressurized and react with hydrogen in a cracking process. An investigation about the trade-off between air pollution, costs and refinery  $CO_2$  emission<sup>6</sup>, states that "deep conversion of residual fuel into lighter low-sulphur shipping fuel is associated with a fuel consumption of about 15 %, compared to about 7 % for conventional refinery processes". Deep conversion of bunker fuels will therefore result in an additional and significant  $CO_2$  emission, which must also be taken into account.

All in all, the additional energy consumptions can be summarized as in Table 1. A more elaborated analysis of the total  $CO_2$  impact is however necessary but is outside the scope of this project. Only the operational impact is considered in Table 1 so also minor contributions from the  $CO_2$  released due to manufacturing, transportation and installation of equipment (scrubbers, refinery columns, etc.) should be included.

	SW scrubbing	FW scrubbing	Low sulphur fuel (0.1 % sulphur)
Pumps	1.0 %	1.0 %	0
Engine back pressure	0.4 %	0.4 %	0
Energy at land	0.0 %	2.0 %	15 %
Total	1.4 %	3.4 %	15 %

Table 1: Additional energy consumption for the different options for reducing  ${\rm SO}_2$  emissions from shipping.

### 2.4 Data acquisition

All sensors, transmitters and analysers listed below are logged each 30 second and stored in 24 hours log files:

- 17 pressure transmitters (water and gas)
- 11 temperature transmitters (water and gas)
- 1 gas analyser measuring SO<sub>2</sub>, CO<sub>2</sub>, and O<sub>2</sub> (gas)
- 2 turbidity analysers (water)
- 2 pH analysers (water)
- 1 PAH analyser (water)
- 8 flow measurements (water)
- 140 0/1 signals for valve position sensors, pumps on/off, etc.

Also the ships GPS position signal is logged.

The data are stored on the ship and on servers at land for documentation and further data analysis.

Molar ratio NaOH required NaOH energy 866 / 41000 =

1.75 Mole NaOH/mole S
 0.048 kg/kg HFO
 866 kJ/kg HFO

2.1 %

# 3 Gas measurements

#### 3.1 Measuring principle

Between 72-120 L/h of sample gas is extracted from the exhaust after the scrubber by aid of a probe. The entire system is designed according to MARPOL ANNEX VI,  $NO_x$  technical code 2008, appendix III. The sample gas passes a 2 micron ceramic filter heated to min. 180°C and is connected with a min. 180°C heated hose to a permeation dryer for removal of water vapour, i.e. the gas components are measured in dry gas to avoid crosssensitivity with water vapour as well as damaging condensate in the analyser. The gas analyser is a Siemens ULTRAMAT 23 NDIR analyser with ranges as specified in Table 2.

Table 2. Stemens OLTRAMAT 25 NDIR analysei			
	Range	Unit	
SO2	0 - 250	ppm (vol/vol), dry	
CO2	0 - 10	% (vol/vol), dry	
O <sub>2</sub>	0 - 21	% (vol/vol), dry	

Table 2: Siemens ULTRAMAT 23 NDIR analyser

The SO<sub>2</sub> and CO<sub>2</sub> cells zero-calibrate automatically each 1 hour with pure dry air. The SO<sub>2</sub> and CO<sub>2</sub> span are checked regularly with a certified (class 1) calibration gas containing 200 ppm SO<sub>2</sub> and 8 % CO<sub>2</sub> in dry N<sub>2</sub>.

The gas measurements have been checked by an accredited company (Force Technology). Their measurements show similar or lower  $SO_2/CO_2$  values than our measurements.

### 3.2 Calculation of fuel sulphur equivalent

In several of the below graphs, the  $SO_2$  and  $CO_2$  measured after the scrubber are converted to an equivalent fuel sulphur level according to MEPC 59, app. II, "proof of the  $SO_2/CO_2$  ratio method":

Fuel S eq. [%, w/w] = 
$$\frac{SO_2[ppm, dry]}{CO_2[\%, dry]} / 43.3 = \frac{SO_2[ppm, wet]}{CO_2[\%, wet]} / 43.3$$

The CO<sub>2</sub> content in the exhaust gas is almost constant (4.3 %) whereby the fuel sulphur equivalent is almost proportional to the SO<sub>2</sub> content. The 1.0 % and 0.1 % S limits correspond to SO<sub>2</sub> concentrations of approx.  $1.0 \times 4.3 \times 43.3 = 186$  ppm and  $0.1 \times 4.3 \times 43.3 = 19$  ppm after the scrubber, respectively.

#### 3.3 SO<sub>2</sub> removal

The amount of  $SO_2$  removal and hence obtained fuel sulphur equivalent is a non-linear function of the water flow to the scrubber, water injection pressure at the jet sprayers, fuel sulfur level, and engine load (MCR). It also depends on whether the scrubber is operating in FW mode or SW mode.

As shown in Figure 6, the sulphur equivalent is approx. 0.07 % at maximum fuel flow and hence engine load. This is significantly below the 0.10 % sulphur limit.

The most important knowledge gained is the data for different engine loads, fuel sulphur content, ship movements, water temperatures, etc. Based on these data, a design program taking into account water chemistry, engine type, fuel data, and ambient conditions has been set-up. This program can now be used to design future scrubbers that can safely meet the 0.10 % S equivalent from 2015 and that – on the other hand – are not over dimensioned with respect to size, water flow rate, and exhaust gas back pressure. The program can also be used to evaluate whether it should be a SW, FW, or a hybrid SW/FW scrubber depending on ship details and route.



Figure 6: Measured fuel sulphur equivalents after the scrubber with a constant water flow to the scrubber of approx. 900 m<sup>3</sup>/h. From the maximum continues rating (MCR) depicted as a factor between 0 at no engine load and 1 at full engine load, the correlation with fuel sulphur equivalence in percentage is easily detected. The chart assembles a journey from Gothenborg to Immingham. As seen from the chart the system operates in FW mode during port transit.

#### 3.4 PM removal

Force Technology, Technological Institute of Denmark, and Copenhagen University were on-board Ficaria Seaways in order to carry out detailed measurements and characterizations of the soot particles in the gas phase before and after the scrubber. Measurements were carried out with a Scanning Mobility Particle Sizer (SMPS) instrument, an Electrical Low Pressure Impactor (ELPI) and a Condensation Particle Counter (CPC). Further characterization of the particles was made in the laboratory with Scanning Electron Microscopy (SEM). In short, the measurements reveal binomial size distributions peaking at around 5-30 nm and again around 50-100 nm. The reduction in number concentration (not mass concentration) is between 31 % and 53 % across the scrubber. These investigations will be published elsewhere as a part of a co-operation project named NaKIM<sup>7</sup>.

Extensive PM measurements were performed on the 1000 kW test rig in Holeby-DK. Here between 45-79 % (w/w) PM removal was measured

according to ISO 8178 (mass based measurements). The highest PM removal efficiency (79 %) was measured with a so-called venturi pre-unit but this was on the cost of an addition pressure drop on 400 mmWC on the exhaust gas (and hence higher  $CO_2$  emission) due to a contraction of the exhaust gas flow. The lowest PM removal efficiencies (45-55 %) were measured with a simple jet-sprayer pre-unit which is not causing any additional back pressure and  $CO_2$  emission. The scrubber on-board Ficaria Seaways is of the jet-sprayer type and is in principle similar to the test installation though scaled up from 1,000 to 21,060 kW.

3.5 NO<sub>x</sub> removal

In the MEPC guidelines (3, § 10.1.5.1) is stated that "the discharge of nitrate should be beyond that associated with a 12 % removal of  $NO_x$  from the exhaust, or beyond 60 mg/L normalized for a washwater discharge rate of 45 tons/MWh (i.e. beyond 2700 g  $NO_3$ /MWh) whichever is greater".

An accredited company (Force Technology) measured NO<sub>x</sub> in the exhaust with an ABB LIMAS 11 UV gas analyser during September 21 and 22, 2010. The concentration was 965 ppm (dry) both before and after the scrubber so there is no measurable uptake of NO<sub>x</sub> in the scrubber water. This is in good agreement with the discharge water samples showing nitrate concentrations corresponding to max 0.2 % NO<sub>x</sub> removal from the exhaust gas. This is well below the limits in the MEPC guidelines<sup>2.3</sup>.

As the scrubber introduces an additional backpressure on the engine, the  $NO_x$  may change. MAN Diesel & Turbo has in connection with on-board performance measurements and on their test bed documented that an additional 15 mbar back pressure will increase the E2-cycle  $NO_x$  from 14.2 g/kWh to max 14.3 g/kWh, at worst conditions. This increase is within the measurement tolerance and still below the IMO  $NO_x$  limit on 17 g/kWh for this type of engine<sup>8</sup>.

# 4 Discharge water analysis

### 4.1 Seawater mode

### 4.1.1 pH

The pH at the water inlet is measured continuously and is approximately 8.1.

At the discharge, the pH will decrease with the amount of  $SO_2$  that has been absorbed per volume of water. This is in agreement with Figure 7, where sulphuric acid have been added to a sample of the inlet water while measuring the pH. The sudden decrease in pH when approximately 1.1 mmol/L of sulphuric acid have been added defines the alkalinity of the seawater. As sulphuric acid contains two acid ions per sulphate ion this corresponds to a seawater alkalinity on 2.2 mmol/L as expected in the North Sea<sup>4</sup>.

pH discharge values between 3.0 and 6.0 have been measured on Ficaria Seaways. As expected, the pH is generally low at high engine load, high sulphur content in the fuel, and low water flow rates to the scrubber.

Even with pH 3, the discharge water is still a very weak acid. In comparison the pH of apple juice is between 2.8 to 3.3. Further to this, the discharge water is quickly mixed outside the ship – especially during voyage – whereby the pH is raised again.



Figure 7: Seawater titrated with sulphuric acid.

### 4.1.2 Turbidity

Turbidity is measured at the water inlet before the main pump and at the outlet after the scrubber. The value is an indication of the waters visual transparency and hence a measure of the amount of insoluble substances in the water. Measurements are made continuously with an Ultraturb Basic SC sensor (range 0-1000 FNU, precision  $\pm 0.008$  FNU or  $\pm 1$  % of the measured values) as well as water samples have been taken out for turbidity measurements by accredited laboratories.



Figure 8: Turbidity in the inlet and discharge water.

According to the MEPC guidelines<sup>2,3</sup>, the discharge water turbidity should not exceed the inlet water turbidity by more than 25 FNU. As seen from Figure 8, the discharge water turbidity is in average only 3 FNU, i.e. significantly below the 25 FNU limit - even without subtracting any value for the inlet water turbidity.

The unexpected high turbidity of the inlet water is believed to be due to air bubbles in the water disturbing the measurements.

To confirm the results, samples from the inlet and discharge water have been analysed by Eurofins DK (accredited laboratory). In average, the inlet turbidity is 2.3 FNU and the discharge turbidity is 4.5 FNU. Other samples were analysed by ASG analytic. These showed an inlet turbidity of 13 FNU and an average discharge turbidity of 3.3 FNU. The higher turbidity in the inlet water than in the discharge water as measured by ASG cannot be explained by air bubbles and we don't have a reasonable explanation for this beside sampling/measurement uncertainties as the values in general are low. However, in any case, all measurements are below the 25 FNU limit.

### 4.1.3 Polycyclic Aromatic Hydrocarbons (PAH<sub>phe</sub>)

The PAH<sub>phe</sub> limit as stated in the MEPC guidelines<sup>2,3</sup> is inverse proportional to the water flow rate and proportional to the engine power output. As examples, the maximum continuous increase in the water should not be greater than 100 ppb at 22.5 m<sup>3</sup>/Mwh, 50 ppb at 45 m<sup>3</sup>/Mwh, or 25 ppb at 90 m<sup>3</sup>/MWh. This makes sense as it will not provide any environmental benefits to dilute the discharge water with clean water or to lower the engine load in case of too high PAH concentrations.

The values measured on Ficaria Seaways are shown in Figure 9. It is noticed that almost a constant level (5-10 ppb) is measured in the period July 2010 to September 2010. As this period cover different engine loads and water flow rates to the scrubber, much more varying  $PAH_{phe}$  concentrations should be expected. The lack of response make no physical sense and is not as intended

in the MEPC guidelines<sup>2.3</sup>. It seriously questions the reliability of the continuous monitoring sensor (TRIOIL, UV fluorescent)<sup>b</sup>.

The reason for the sudden increase in PAH level in October and November 2010 is unknown so in December 2010, the PAH<sub>phe</sub> sensor was taken from the ship and send to the supplier for maintenance and calibration. However, the sensor was okay and was not in need of calibration according to the supplier. The sensor was installed again in January 2011.



Figure 9: PAH levels measured with the continuous monitoring sensor.

 $PAH_{phe}$  measurements on extracted water samples, analysed by ASG analytic (accredited laboratory) show total  $PAH_{phe}$  concentrations in the SW inlet of 0 ppb and discharge concentrations in the range of 0.5 - 0.7 ppb<sup>c</sup> at 50 m<sup>3</sup>/MWh. These measurements are much more reliable and far below the 25 ppb indicated by the analyser at the time of sampling.

It is believed that much of the  $PAH_{phe}$  could be trapped within the soot particles. In the laboratory, possible  $PAH_{phe}$  in the soot is extracted with hexane so it can be reliable detected by gas chromatography. Even in the laboratory, the PAH concentrations are below or close to the detection limits.

The above observations and troubles associated with a continuous PAH measurement on-board a ship has also been experienced and reported by Wärtsila<sup>9,10</sup>.

#### 4.1.4 Suspended Solids

Samples were taken out in January 2011 while the ship operated at 85 % MCR and in SW mode with 980 m<sup>3</sup>/h of water. The samples were analysed by ASG analytic for their content of suspended particular matter before and after the scrubber.

The results show that the inlet water contains less than the detection limit, while the discharge water contains approximately 2.75 mg/L. By multiplying

<sup>&</sup>lt;sup>b</sup> The flow of sample water to the PAH sensor has been checked regularly. This can also be seen on the discharge pH sensor which is connected in serial with the PAH sensor and which is responding as expected on process changes.

<sup>&</sup>lt;sup>c</sup> Mainly naphthalene, fluorene and phenanthrene.

these numbers with the waterflow, it is calculated that the scrubber in this case captures 2.7 kg/h of PM corresponding to 0.15 kg/MWh.

### 4.1.5 Oil in Water

Samples of water were taken out in SW mode before and after the scrubber while operating on both high sulphur and low sulphur HFO. These samples were analysed by ASG analytic for hydrocarbons with chain lengths between 10 and 40.

The MEPC guidelines<sup>2,3</sup> do not contain any limits for oil in water. However for comparison purposes normal requirements for bilge water has a maximum of 15 ppm. The actual limit stated by the Danish authorities in the dispensation for the scrubber on Ficaria Seaways is 5 ppm. The above measurements are well below this limit.

Table 3: Off in water results. Measured chain rengths are cito-c40°.				
Position	[mg/L] = [ppm]	[mg/kWh]		
SW inlet	1.4	74		
SW discharge 1.0 % HFO	1.2	65		
SW discharge 2.2 % HFO	1.9	101		

Table 3: Oil in water results. Measured chain lengths are C10-C40<sup>d</sup>.

## 4.1.6 Nitrate

Samples of the discharge water were taken out and forwarded to Eurofins DK for nitrate and nitrite determination. The inlet water contains  $0 - 5.9 \ \mu g \ N/L$ . Depending on the engine load and water flow through the scrubber, the discharge water contains between 31 - 130  $\mu g \ N/L$ . The highest concentration of nitrate was found in a sample taken out at 95 % MCR (September 21, 2010, at 14.30). The concentration was 130  $\mu g \ N/L$  corresponding to 0.028 g  $NO_3$ /kWh or 0.021 g  $NO_2$ /kWh. This is well below the MEPC limit on 60 mg/L normalized for a washwater discharge rate of 45 tons/MWh (i.e. beyond 2700 g  $NO_3$ /MWh) and in good agreement with the gas phase measurements showing no measureable NOx removal in the scrubber (see section 3.5).

## 4.1.7 Heavy metals

Samples of the discharge water were taken out and forwarded to Eurofins DK for heavy metal analysis. All samples were taken out in seawater mode with the engine operating on HFO containing 2.2 % sulphur. The fuel oil consumption varied from 1.700 - 3.900 L/h and the water flow from 780-980 m<sup>3</sup>/h. The results are summarized in Table 4.

Trace	SW Inlet	v	SW discharge	
Element	[µg/kg]	[mg/MWh]	[µg/kg]	[mg/MWh]
Vanadium	1.1	77	164	10302
Nickel	2.2	231	43.3	2818
Chrome	0.8	68	5.6	429
Cadmium	0.1	6	0.1	4
Mercury	< 0.05	0	< 0.05	0
Led	13.3	904	26.4	1569
Arsen	1.2	105	1.4	88
Copper	74.4	5120	190	11776
Zinc	124	8492	324	20727

Table 4: Average concentrations of heavy metals in the inlet and discharge water.

<sup>d</sup> ppm = mg/L if assuming a water density on 1 kg/L.

|--|

As seen in table 5, especially vanadium, nickel, copper and zinc are collected in the water. The difference between total heavy metals in discharge and inlet water is 33 g/MWh and thus comparable to the input on 44 g/MWh from the fuel oil to the engine (Table 5). For the current engine operating maybe 70.000 MWh per year, the 33 g/MWh becomes 2310 kg/year. No corrosion is seen on the high grade steel in the scrubber (containing nickel etc.) so the source is the fuel oil.

4.2 Fresh water mode

In order to balance pH and thereby the uptake of  $SO_2$  from the exhaust gas, sodium hydroxide (NaOH) is continuously added to the water. In practice, it has been found that 1.75 mole NaOH is required per mole of sulphur in the fuel oil.

When necessary the water in the system can be cleaned by aid of a centrifuge from Alfa Laval and then returned back into the closed loop system or discharged to the sea.

## 4.2.1 pH

In freshwater mode, the pH value is controlled by the amount of NaOH added to the water. Normally, the discharge pH is kept above 6.5.

## 4.2.2 Turbidity

ASG analytic has analysed several water samples taken before and after the Alfa Laval prototype centrifuge. The results showed an average of 315 FNU before and 5 - 77 FNU after the centrifuge.

Subsequently the water cleaning system has been upgraded (November 2011) to improve the cleaning efficiency and reliability and which now enables the system to comply with the 25 FNU limit. Figure 10 shows the water cleaning unit on-board Ficaria Seaways.



Figure 10: The centrifuge is a high speed separator. The dirty water is feed in through the top with a turbidity of approx. 250 FNU and the clean water leaves the separator

below the feed pipe with a turbidity of approx. 10 FNU. The separated sludge is shot from the separator into a collecting tank (shown at the side of the centrifuge with the u-bended pipe piece).

### 4.2.3 Polycyclic Aromatic Hydrocarbons (PAH<sub>phe</sub>)

Water samples were taken out January 18, 2011 after the water cleaning centrifuges and analysed for PAH<sub>phe</sub> by ASG analytic. The levels are between 0.52 and 1.31 ppb. This is extremely low concentrations, well below the MEPC limit<sup>2.3</sup>, and for most of the PAH species, below the detection limit of the gas chromatograph applied by the laboratory. It is impossible to quantify such low concentrations with any continuous monitoring equipment on-board a ship.

### 4.2.4 Heavy metals

Table 5 shows the heavy metal content in the fuel oil, sludge collected from the centrifuge, and cleaned discharge water.

### 4.2.5 Nitrite and nitrate

Water samples were taken January 18, 2011 of water that had been circulated for 5½ hours without discharge. The main engine delivered 57 MWh of power during this period. The content of nitrite  $(NO_2)$  and nitrate  $(NO_3)$  increase from 0 mg/L in the clean water to 153 mg/L nitrite and 63 mg/L nitrate in the circulated water. As also found in SW mode, this is significantly below the  $NO_x$  and nitrate limits in the MEPC guidelines<sup>2,3</sup>.

	HFO		Centrifuge Sludge		Discharge water	
	2.	2 % S				
Laboratory	A	ASG	Eu	irofins	A	ASG
Unit	[mg/kg]	[mg/MWh]	[mg/kg]	[mg/MWh]	[mg/L]	[mg/MWh]
Vanadium	155	28675	6600	5315	3	1105
Nickel	47	8695	4000	1911	< 1 (d.l)	< 368 (d.l)
Chrome	3	555	250	121	< 1 (d.l)	< 368 (d.l)
Cadmium	3	555	< 0.05	84	< 1 (d.l)	< 368 (d.l)
Silicon	9	1665	n/a	n/a	< 1 (d.l)	< 368 (d.l)
Iron	22	4070	n/a	n/a	< 1 (d.l)	< 368 (d.l)
Mercury	n/a	n/a	0.03	0	< 1 (d.l)	< 368 (d.l)
Led	n/a	n/a	43	6	< 1 (d.l)	< 368 (d.l)
Arsen	n/a	n/a	6	1	< 1 (d.l)	< 368 (d.l)
Copper	n/a	n/a	780	117	< 1 (d.l)	< 368 (d.l)
Zinc	n/a	n/a	370	56	< 1 (d.l)	< 368 (d.l)
Total		44215		7611		n/a

Table 5: Heavy metal analyses of heavy fuel oil, sludge and discharge water. Samples taken January 18-19, 2011.

# 5 Discussion

The scrubber on-board Ficaria Seaways was designed as an hybrid scrubber in order to get more experiences with FW and SW scrubbing and to better evaluate advantages and disadvantages of the two methods.

The main environmental concern regarding PM emissions from shipping is the ability of the ultrafine part of the particles to penetrate into human lungs if emitted together with the exhaust gas to the atmosphere. Much of the ultrafine particles are caused by  $SO_2$ , which oxidizes to  $SO_3$  and forms secondary aerosols in the atmosphere. By removing the  $SO_2$ , formation of secondary aerosols and acid rain are avoided. For both SW and FW scrubbing, the gaseous  $SO_2$  can be removed with efficiencies close to 100 %. The  $SO_2$  is converted to sulphate and discharged to the sea, which already contains much larger amounts of sulphate.

From an overall environmental perspective, the main advantage of SW scrubbing is that it is not consuming sodium hydroxide. Sodium hydroxide is produced by electrolysis of concentrated salt water – typically requiring 5000 kWh/ton<sup>5</sup>. As calculated (Section 2.3), this corresponds to 1 % of the energy in the HFO per % of sulphur in the HFO.

The main advantage of FW scrubbing is that only a very small water flow has to be discharged whereby it is possible to clean this water in an efficient manner. On Ficaria Seaways, only about  $2 - 4 \text{ m}^3$ /h is discharged for the FW mode operation while up to 1000 m<sup>3</sup>/h is discharged in SW mode. However, the data from Ficaria Seaways has shown that the amount of soot in the SW is so limited that the turbidity measurement and PAH content are below the limits in the MEPC guidelines<sup>2,3</sup>.

The soot (PM) collected in FW mode (about 0.15 kg/MWh) mainly consists of unburned hydrocarbons but it also contains heavy metals – especially vanadium and nickel are detected. The soot is collected on-board and pumped to reception facilities in port. The heavy metals originate from the fuel oil and the carbon part is unburned fuel / lube oil.

# 6 Abbreviations

d.l.	Detection limit
n/a	Not analysed
CPC	Condensation Particle Counter
ECA	Emission Control Area
ELPI	Electrical Low Pressure Impactor
FNU	Formazin Nephelometric Unit
FW	Freshwater
G	Gravitation Force = $9.8 \text{ m/s}^2$
HFO	Heavy Fuel Oil
IMO	International Maritime Organization
MARPOL	International Convention for the Prevention of Pollution
73/78	From Ships, 1973 as modified by the Protocol of 1978
MCR	Maximum Continuous Rating (on the engine)
MEPC	Marine Environmental Protection Committee
NaOH	Sodium hydroxide, Caustic soda
$PAH_{_{\mathrm{phe}}}$	Polycyclic Aromatic Hydrocarbon, phenantrene
	equivalence
PM	Particular Matter (soot particles)
SEM	Scanning Electron Microscopy
SMPS	Scanning Mobility Particle Sizer
SW	Seawater

# 7 References

<sup>5</sup> http://www.olinchloralkali.com/Library/Literature/OverviewOfProcess.aspx (2011)

<sup>6</sup> Hein de Wilde, Pieter Kroon, Cleaner Shipping: Trade off between air pollution, costs and refinery CO2 emissions, Energy research Centre of the Netherlands,

<sup>7</sup> http://www.nakim.dk/ (2011)

<sup>8</sup> MAN Diesel, Temporary Add to IAPP Certificate, Engine type L60MC-C, Copenhagen, June 18 2009

 $^{\rm 9}$  Wärtsila, Exhaust Gas Scrubber Installed On-board MT "SUULA", Public Test Report, June 20, 2010.

<sup>10</sup> Wärtsilä Finland Oy, Polycyclic Aromatic Hydrocarbon (PAH) measurements from the effluent of an Exhaust Gas Cleaning System (EGC), June 15, 2010.

 $<sup>^{\</sup>scriptscriptstyle 1}$  Don Gregory, Exhaust Gas Cleaning System Association (EGCSA), EGCS Handbook, 2010

<sup>&</sup>lt;sup>2</sup> IMO Resolution MEPC.170(57)

<sup>&</sup>lt;sup>3</sup> IMO Resolution MEPC.184(59)

<sup>&</sup>lt;sup>4</sup> <u>http://en.wikipedia.org/wiki/Alkalinity</u>

#### Summary

An exhaust gas scrubber able to remove SO2 has been installed in July 2009 as a retrofit onboard the DFDS vessel Ficaria Seaways (Tor Ficaria until July 2011) after a MAN 21 MW 2-stroke engine. The exhaust gas scrubber is able to operate in both a seawater (SW) and a fresh water (FW) mode and it has been tested while the ship was in normal operation. It has been in operation for 5630 hours (June 2012). The obtained results show, that it is possible to reduce the SO2 level to under 19 ppm in the exhaust gas. This corresponds to below 0.1 % sulfur in the fuel whereby it is possible to comply with IMO's most strict sulphur requirement, which will prevail from January 2015.

En scrubber til rensning af udstødningsgas for SO2 er blevet installeret i juli 2009 som retrofit efter en MAN 21 MW 2-takts motor ombord på DFDS skibet Ficaria Seaways (Tor Ficaria indtil den 22. juli 2011). Skrubberen kan operere både med havvand (SW) og ferskvand (FW) og er blevet testet, mens skibet var i normal drift. Den har været i drift i 5630 timer (juni 2012). De opnåede resultater viser, at det er muligt at reducere SO2 emissionen til under 19 ppm. Dette svarer til under 0,1 % svovl i brændstoffet, hvorfor det er muligt at overholde IMO's strengeste svovlkrav, der vil komme til at gælde fra 1. januar 2015.



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