

SEAWATER SO₂ SCRUBBING IN A SPRAY TOWER FOR MARINE APPLICATION

G. Caiazzo*, G. Langella, F. Miccio*, F. Scala***

scala@irc.cnr.it

* Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche,
Piazzale Vincenzo Tecchio 80, 80125 Napoli, Italy

** DIME, Dipartimento di Ingegneria Meccanica per l'Energetica, Università degli Studi di
Napoli Federico II, Via Claudio 21, Napoli 80125, Italy

Abstract

A seawater spray scrubber was set up and tested with focus on desulfurization of marine engine exhaust gas. Experimental tests were carried out simulating typical exhaust conditions of a marine diesel engine burning heavy fuel oil, and using real seawater. Different flue gas flow rates, seawater flow rates, and SO₂ concentrations were tested. Liquid-to-gas ratios were in the range $1-10 \times 10^{-3}$. A comparison between seawater and distilled water was also carried out, to elucidate the effect of seawater alkalinity. In all conditions the liquid phase was analyzed for alkalinity, pH, and sulfate content before and after the tests. Finally, the spray droplet size distribution was measured as a function of the liquid flow rate.

Experimental results indicated that seawater performed better than distilled water, by exploiting its inherent alkalinity. The desulfurization performance improved by increasing the liquid flow rate and gas residence time, and by decreasing the SO₂ concentration. SO₂ capture efficiencies up to 93% were measured under the present operating conditions.

Introduction

Seawater SO₂ scrubbing (SWS) is a promising alternative to the use of Marine Diesel Oil (MDO) and Marine Gas Oil (MGO) fuels in shipping; international regulations (IMO Annex VI of MARPOL 73/78 [1]) put heavy limits on the maximum sulfur amount in marine fuels in order to reduce SO₂ emissions at the ship stack. Fuel cost represents one of the heaviest voices in ship budget, and switching from Heavy Fuel Oil (HFO, 3.5–4.5% S w/w) to MDO (1.0% S w/w) or MGO (0.1% S w/w) would imply a significant increase of costs. Presently, HFO with a maximum content of 3.5% S w/w is still allowed outside SECAs (Sulfur Emissions Control Areas), whereas MDO is mandatory inside SECAs. On January 1st 2015 the maximum allowed % S w/w will be decreased to 0.1% (MGO), and on January 1st 2020 burning HFO will be not allowed anymore. Moreover, while MDO can be produced by mixing HFO and a lower sulfur content fuel, MGO production needs different and more complex technologies; in fact, no fuel-mixing is possible to produce MGO, neither actual sulfur removal techniques are good enough to obtain an almost totally sulfur-free fuel.

Literature concerning fuel switch in ships and possible post-combustion DeSOx processes in the marine field is very poor despite SWS has been widely discussed as a future solution for ships. In fact, it has been suggested that SWS is an economically attractive solution, where scrubbing performance relies on seawater natural alkalinity [2,3]. The advantages of using seawater involve simple plant design, no addition of chemicals and no solid by-products. The acidified effluent can be discharged directly into the sea, after a neutralization step by mixing with fresh seawater and additional forced oxidation of sulfite ions by air blowing.

The use of seawater for SO₂ scrubbing has long been recognized as a viable technology in the case of coal power plants. Oikawa et al. [4] describe the technical and environmental aspects of a seawater wet scrubber used as an FGD device for a 600 MWe carbon power plant in China. Three different boiler loadings were considered using a low sulfur content coal, and an SO₂ removal efficiency of 95-98% was achieved in a perforated plate scrubber. Similar figures were reported by Williams [5], who described an experimental test of SWS carried out in a low sulfur coal plant. Chemical and physical features of the seawater-SO₂ interaction are described by Sun et al. [6], who focused on a membrane contactor scrubber.

Only few reports are available where SWS was performed on a real working ship, and most of these reports come from industries involved in SO₂ scrubber production. An interesting experimental report was issued by BP Marine [7] on the desulfurization efficiency of a SWS plant installed on the “Pride of Kent” ship. The scrubber was installed for a 1 MW auxiliary engine, recording a removal efficiency of nearly 100% corresponding to a 36 m³/h water flow. Seawater pH values after scrubbing the exhaust gas from the engine were also recorded: seawater pH at the scrubber exit resulted to be much lower than at the inlet, due to the interaction with the acid gases in the exhaust gas. Kircher et al. [8] reported on a monitoring campaign of a SWS scrubber installed on a 7.2 MW ship burning HFO. SO₂ and PM emissions were monitored, and the SO₂ removal efficiency was about 75%.

Specific requirements for maritime SO₂ scrubbing systems include: low energy consumption and pressure drop, simplicity and adaptability to existing equipment, stability and easiness of control. One possible candidate technology meeting these requirements is spray scrubbing, which is known to be an effective technology for the desulfurization of fuel oil flue gas [9]. Caiazza et al. [10] recently presented a spray scrubber model focused on the use of seawater under marine diesel engine exhaust conditions. Results showed that natural seawater alkalinity and internal circulation in the droplets assure an enhanced SO₂ absorption from the gas-phase. To comply with the MARPOL limits the amount of scrubbing seawater was found to be conspicuous, implying large dimensions of the scrubbing tower.

This paper reports on the setup of a seawater spray scrubber and on the experimental tests carried out under typical exhaust conditions of a marine diesel engine burning heavy fuel oil. SO₂ capture experiments were carried out using real seawater picked up at about 1000 m from the Naples coast and distilled water, for comparison.

Experimental

The scrubbing tower is a stainless steel tube with 160 mm diameter and 1880 mm height. The column is equipped with six thermocouples for measurement of the temperature profile along the height, and is externally insulated. Air is blown by a compressor and heated up to about 250°C by an electric resistance heater. Typical temperature range of exhaust gas at ship stack is about 200-500°C. After heating, air enters a toroidal shaped mixing chamber at the bottom of the column, where it mixes with a stream of N₂-SO₂. The total gas flow rate has been fixed to either 40 m³/h or 60 m³/h, corresponding to an approximate gas residence time in the reactor of 4.3 s and 2.9 s, respectively. SO₂ inlet concentrations in the range 500-1000 ppm were used, corresponding to typical concentrations obtained in diesel engine exhaust when burning HFO (sulfur content in the range 2.5-4.5% w/w). The gas flow exits the column at the top and a small flow (0.06 m³/h) is sucked by a membrane pump and sent to a NDIR digital SO₂ analyzer.

Once steady conditions are reached, water is pumped to the top of the scrubbing tower from a 0.5 m³ tank. The liquid flow was in the range 0.06-0.4 m³/h, corresponding to liquid-to-gas ratios in the range 1-10 x 10⁻³. During the counter-current interaction between gas and liquid flows, gas is cooled and moisturized because of water evaporation while SO₂ is absorbed in the liquid. Post-scrubbing water is collected in an accumulation tank at the bottom of the column and is pumped to a return-tank, where water samples are taken for a following chemical analysis. The SO₂ capture efficiency is calculated for each run after steady conditions are achieved by comparing the outlet SO₂ concentration to the inlet SO₂ concentration measured before sending water inside the scrubber.

One device with multiple orifices was installed centerline for water injection at the top of the scrubber. It produces a 60° angle spray with the water flow rates used in the present work. Considering the column diameter, this implies that a fraction of the spray impacts on the column wall and generates a downward moving water layer at the wall. An analysis of the droplets dimensions has been carried out *ex situ* by means of a fast camera and a halogen lamp illuminating the spray. After calibration of the data analysis software with a reference gauge, for each liquid flow rate a 30 s video was performed at 90 frames/s. Droplets in the frames appear as black on a white background, allowing the software to measure their size by contrast. About 1000 frames have been analyzed for every liquid flow rate. Mean size, variance, standard deviation, variation coefficient have been estimated for each data set, whereas distribution asymmetry has been analyzed by estimating skewness. In particular, moving from 0.4 m³/h to 0.1 m³/h, the droplet mean size grows from 0.4 to 0.9 mm, since the larger is the flow rate the higher is the pressure at the nozzle. It is important to recall that the droplet dimension has a direct influence on the absorption process, because larger droplets are associated to lower specific surface areas. In addition, too small droplets (< 0.2 mm) should be avoided, since the gas flow would entrain the droplets out of the column.

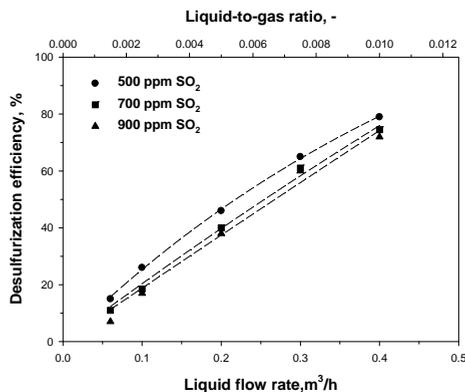


Figure 1. Desulfurization efficiency results with distilled water at different liquid flow rates and SO₂ inlet concentrations. Gas flow rate = 40 m³/h.

Results

The first experimental campaign was directed to elucidate the effect of the liquid flow rate on the scrubber desulfurization efficiency at a fixed gas flow rate (40 m³/h). Three different inlet SO₂ concentration levels were tested, namely 500, 700 and 900 ppm. The water flow rate was varied in the range 0.06-0.4 m³/h. Tests were repeated with both seawater and distilled water, for comparison.

Figure 1 reports the desulfurization results obtained with distilled water. It is important to underline that while the original distilled water had negligible alkalinity, this was not true for the distilled water after its pouring in the tank, since CO₂ rapidly dissolved in water after contact with air. As a consequence, the used distilled water had a non-negligible alkalinity, as measured by chemical analysis (Table 1). It is reminded here that the bicarbonate ion ([HCO₃⁻]) represents the dominating contribution to water alkalinity. Consequently, the desulfurization efficiency was relatively high, larger than could be expected for pure physical absorption of SO₂ in water. As expected, the desulfurization efficiency increased with the liquid flow rate and decreased with the inlet SO₂ concentration. The largest efficiency was 79%, at 0.4 m³/h water flow rate and 500 ppm SO₂.

Table 1. Results of water chemical analysis. Spent samples collected after tests at 40 m³/h gas flow rate, 0.4 m³/h water flow rate.

	Fresh distilled water	Spent distilled water	Fresh seawater	Spent seawater
Alkalinity [g/m ³]	155	< 10	230	< 10
Sulfates [g/m ³]	28	335 ± 10	2225	3085 ± 25
pH	6.95	2.84 ± 0.05	7.85	2.83 ± 0.1

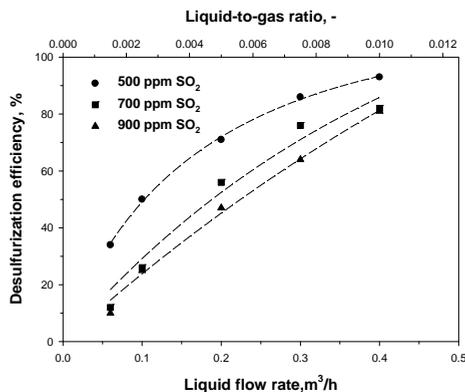


Figure 2. Desulfurization efficiency results with seawater at different liquid flow rates and SO₂ inlet concentrations. Gas flow rate = 40 m³/h.

Figure 2 reports the desulfurization results obtained with seawater under the same experimental conditions. Clearly, seawater performs better than distilled water as a consequence of the larger alkalinity. The same trends of the efficiency with liquid flow rate and SO₂ concentration as for distilled water were observed. In this case the largest efficiency was 93%, again at 0.4 m³/h water flow rate and 500 ppm SO₂. The second experimental campaign was carried out with seawater only by fixing a larger gas flow rate (60 m³/h), corresponding to a shorter residence time in the scrubber (2.3 s instead of 3.4 s). The water flow rate was varied in the same range as in the previous tests, while the three inlet SO₂ concentration levels of 500, 750 and 1000 ppm were used. Note that the same liquid flow rate corresponds to a lower liquid-to-gas ratio when compared to the previous test campaign.

Figure 3 reports the desulfurization results obtained in the tests with a shorter gas residence time. Results show lower desulfurization efficiencies at the same liquid-to-gas ratios, because of the shorter gas-liquid contact time. Again, similar trends of the efficiency with liquid flow rate and SO₂ concentration were observed. The largest efficiency was 77%, at 0.4 m³/h water flow rate and 500 ppm SO₂.

Both seawater and distilled water samples before and after scrubbing were analyzed for alkalinity, pH and sulfates, as shown in Table 1. The post-scrubbing samples were collected after desulfurization tests carried out with a liquid flow rate of 0.4 m³/h. Since there was no remarkable effect of the SO₂ concentration level on the analysis results, data at different SO₂ levels were lumped together.

The fresh distilled water and seawater had 155 and 230 g/m³ alkalinity, respectively. On the other hand, all the samples after SO₂ scrubbing had an alkalinity below detection limit. As regards sulfate content, fresh distilled water obviously had a very low sulfate concentration, while fresh seawater had a very high content. After the desulfurization tests the sulfate content increased in all samples. The increase was larger for the seawater samples, consistently with the larger SO₂ capture efficiency.

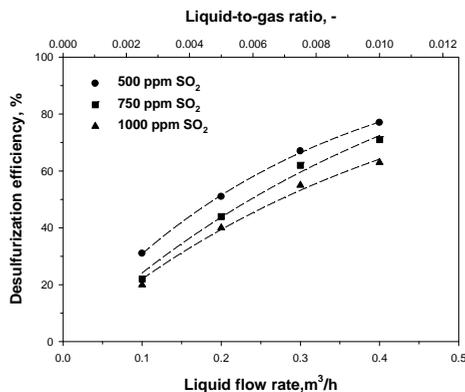


Figure 3. Desulfurization efficiency results with seawater at different liquid flow rates and SO₂ inlet concentrations. Gas flow rate = 60 m³/h.

A very important measured variable is pH, since post-scrubbing water is acidified due to the SO₂ absorption process. Both fresh samples had a pH value around 7-8, while the post-scrubbing samples had all pH < 3. Thus, in marine applications, spent seawater needs to be further treated before it can be discharged in sea.

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