Article

Modeling and Simulations of NO\textsubscript{x} and SO\textsubscript{2} Seawater Scrubbing in Packed-Bed Columns for Marine Applications

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Abstract: Seawater scrubbing of nitrogen oxides and sulfur oxide from marine emissions was simulated in packed-bed columns exposed to static inclination and heaving/oscillating motions. Fourth generation random packings (Raschig super-Rings) while providing much smaller pressure drop than traditional Pall-Rings ensure comparable absorption efficiency for the pollutants. Complete removal of SO\textsubscript{2} was predicted over the tested pressure range with absorption efficiency indifferent to scrubber inclination or heaving/oscillating motions. In contrast, NO\textsubscript{x} and CO\textsubscript{2} absorptions are negatively impacted for inclined seawater scrubbers. Removal efficiency is not lowered significantly owing to larger scrubber pressure and because diffusion of N\textsubscript{2}O\textsubscript{4} into the liquid phase is associated with a rapid pseudo first-order reaction. The asymmetrical oscillating motion of the scrubber degrades the removal performance which exhibits wavy patterns close to the steady-state solution of the average inclination angle. NO and CO\textsubscript{2} absorption performance waves are moving toward a steady-state solution of vertical scrubber when the asymmetry of the two inclined positions of the scrubber downgrades. Symmetric oscillation and heaving motion led to performance disturbance waves around a steady-state solution of the vertical scrubber which are determined by the parameters of angular/heaving motion.

Keywords: marine packed-bed columns; gas-liquid countercurrent flow; simultaneous SO\textsubscript{2} and NO\textsubscript{x} absorption; 3-D model; scrubber performance

1. Introduction

Marine shipping represents more than 90% of the whole international commerce [1] and is the highest energy-efficient way for long-distance transport. However, the shipping emissions affect significantly the ocean ecosystems and human health [2]. Sulfur and nitrogen oxides, and particulate matter emissions from marine diesel engines have a significant impact on the environment and are moved to a certain extent over the continental land where they enhance the ground-based pollutant load. SO\textsubscript{2} initiates acid rains and NO\textsubscript{x} emissions generate photochemical smog, which increases the level of ozone in the lower atmosphere, and dangerous organic compounds [3]. Particulate matter (condensed hydrocarbons and sulphates) can insert in the lungs and attempt the circulation system, giving cardiovascular and pulmonary illnesses [3].

Sulfur and nitrogen oxides can be eliminated from the exhaust gas via typical selective catalytic/non-catalytic reduction and flue gas desulfurization processes [4–6] which enhance the complexity of the equipment, the capital cost and the energy need [5]. Additionally, the selective catalytic reduction is challenged by the deactivation of the catalyst by SO\textsubscript{2} and selective non-catalytic reduction needs elevated temperatures (900–1000 °C) with complex temperature control to prevent
ammonia slip and to conclude the NO\textsubscript{x} removal process. Alternatively, the removal of NO\textsubscript{x} and SO\textsubscript{x} involves processes that apply the nitric and sulfuric acid chemistry. Keilin and Wallit [7] proposed a process where, in the presence of NO\textsubscript{2}, SO\textsubscript{2} is oxidized to SO\textsubscript{3} which is absorbed in water in a sulfuric acid absorber. The recycled sulfuric acid is utilized to absorb NO and directed in a catalytic stripping column where NO is oxidized to NO\textsubscript{2}. NO\textsubscript{2} generated in the catalytic stripping column is reprocessed in SO\textsubscript{2} oxidation reactor or removed, the excess, as HNO\textsubscript{3} in a nitric acid absorber. White et al. [8] suggested a low-temperature process that removes sulfur and nitrogen oxides in two absorption columns connected in series. Direct oxidation of NO to NO\textsubscript{2} at high pressure replaces NO catalytic oxidation. The first absorption column works at intermediate pressure and is mainly in charge of SO\textsubscript{2} absorption and the second absorption column removes the non-absorbed NO\textsubscript{2} at high pressure. Iloeje et al. [5] modified this two-column process design with a single reactive absorption column operated at high pressure which succeeds the complete removal of SO\textsubscript{x} and NO\textsubscript{x}.

In the above-mentioned land-based NO\textsubscript{x} and SO\textsubscript{x} removal processes, water can be substituted with seawater and sulfur and nitrogen oxides removal by scrubbing can be applied on marine ships. The major advantage of performing with seawater includes the simultaneous elimination of NO\textsubscript{x} and SO\textsubscript{2} from exhaust gas, undemanding plant design, compact scrubber system, no chemicals and absence of solid by-products. Furthermore, in the case of open loop scrubbers the acidified effluent is discharged into the ocean after neutralization [9]. Additionally, seawater scrubbers working under pressure excludes the losing of marine engines power because of the backpressure (no need to compensate the backpressure as in the case of seawater scrubbers operated at atmospheric pressure). Moreover, at high pressure SO\textsubscript{2} is totally removed even if the content of sulfur in the fuel is larger than 3.5%. SO\textsubscript{2} seawater scrubbing becomes a promising alternative for marine applications, which allows for the use of Heavy Fuel Oil as a substitute of high-priced low sulfur fuels, such as Marine Diesel Oil or Marine Gas Oil imposed by International Maritime Organization which established stringent limits on NO\textsubscript{x} and SO\textsubscript{x} emissions of marine diesel engines [10,11]. In marine shipping the fuel cost is two-thirds of the total transportation cost, explaining while the substitution of Heavy Fuel Oil (3.5–4.5% w/w S) with Marine Diesel Oil (1.0% w/w S) or Marine Gas Oil (0.1% w/w S) would involve a substantial increase of costs [1,6].

A limited number of studies have been focusing on the sulfur and nitrogen oxides removal from marine emissions. Andreasen and Mayer [12] studied SO\textsubscript{2} seawater scrubbing of marine engine exhaust gas at different values of SO\textsubscript{2} concentration, seawater temperature, alkalinity and salinity and noticed that SO\textsubscript{2} absorption capacity reduces with the decline of alkalinity and salinity and SO\textsubscript{2} removal capacity of normal seawater is approximately two times larger than of brackish water. Moreover, Darae et al. [13] studied experimentally and theoretically SO\textsubscript{2} seawater scrubbing of flue gas from industrial plants in a countercurrent packed-bed column and found that liquid and gas flow rates, gas temperature and SO\textsubscript{2} concentration affect significantly SO\textsubscript{2} removing efficiency. Nielsen et al. [1] exposed the modeling and design of an ingenious marine machinery system, with potential in marine applications concerning both the environment and energy, which incorporates a waste heat recovery system and the removal of SO\textsubscript{2} via a wet sulfuric acid process. Tang et al. [14] investigated the desulphurization efficiency of a magnesium-based seawater scrubber on-board large marine ships and found that the ratio between the liquid and gas flow rates and pH are key parameters influencing the desulphurization efficiency. Flaggiello et al. [9] analyzed experimentally and theoretically SO\textsubscript{2} removal from flue gas in a seawater packed-bed column filled with a structured packing (Mellapak 250X) at 0.1 MPa and 25 °C. Yang et al. [6] proposed the removal of NO\textsubscript{x} and SO\textsubscript{2} from ship emissions in a semi-continuous bubble column reactor using electrolyzed seawater. The results illustrate that NO\textsubscript{x} removal efficiency can be improved by the increase of the inlet NO concentration, the concentration of CO\textsubscript{2} and O\textsubscript{2} (coexisting gases), reaction temperature and active chlorine concentration, but is impeded by the increase of the gas velocity.

However, there are important operative and technical challenges to managing sulfur and nitrogen oxides removal on-board large marine ships and offshore processing platforms, the one more
noticeable being the impact of weather and ocean conditions on the performance of absorption process. Packed-bed columns for seawater scrubbing of marine engine exhaust gas on-board large marine ships and floating production, storage and offloading (FPSO) nonstationary platforms may be defined by the ocean physical constraints (ocean state, surface ocean currents because of the wind, wind waves and weather variables) via heaving and angular ship motions which could possibly change the seawater scrubber functioning [15–17]. Therefore, the best design of absorption packed-bed columns working in changeable ocean conditions requests for advanced comprehension and quantification of the hydrodynamics, mass and energy transport associated with the reaction kinetics and thermodynamics [15,16]. Furthermore, the exploitation of offshore seawater scrubbers demands corrective design measures to preempt, or to compensate for, any deviation in removal efficiency with respect to conventional onshore sulfur and nitrogen oxides removal units [18].

Even if the progression realized in the modeling and design of sulfur and nitrogen oxides removal from the marine exhaust gas is evident none of the available investigations attempted to explore the case of NOx and SOx seawater scrubbing in packed-bed columns on-board large marine ships or offshore floating nonstationary platforms. This study presents an analysis about the performance of simultaneous removal of SO2, NOx and CO2 (coexisting gas) by seawater scrubbing in countercurrent random packed-bed columns exposed to static inclination and rolling/heaving motion (Figure 1) via a Eulerian 3-D dynamic model. The performance attained in inclined and oscillating/heaving seawater scrubbing packed-bed columns is compared with the removal efficiency in a standard vertical column. The impact of angular/heaving motion parameters on gas-liquid flow hydrodynamics and removal efficiency is highlighted.

Figure 1. Configuration of seawater scrubber: (i) Vertical scrubber, (ii) inclined scrubber, (iii) scrubber under heaving motion, (iv) oscillating scrubber between two symmetrical inclined positions, (v) oscillating scrubber between the vertical and an inclined position, (vi) oscillating scrubber between two asymmetrical inclined positions.
2. Mathematical Model

2.1. Hydrodynamic Model

The hydrodynamic platform is the basis of the more complex model of countercurrent random packed-bed columns on-board marine ships and offshore floating units used for the simultaneous seawater absorption of SO$_2$, NO$_x$ and CO$_2$. A Eulerian 3-D model was proposed for two-phase unsteady flow (assumed annular and separated) in vertical, inclined and oscillating heaving motion, the axial momentum balance equations were amended with the heaving acceleration term. The model has been presented elsewhere [22,24–26] and is only succinctly summarized here:

- Continuity and momentum balance equations for the incompressible and viscous Newtonian liquid phase,

\[
\frac{\partial}{\partial t} (\rho \varepsilon_t) + \frac{\partial}{\partial z} (\rho \varepsilon_t u_{z,t}) + \frac{1}{r} \frac{\partial}{\partial r} (r \rho \varepsilon_t u_{r,t}) + \frac{1}{r} \frac{\partial}{\partial \theta} (\rho \varepsilon_t u_{\theta,t}) = 0, \tag{1}
\]

\[
\frac{\partial}{\partial t} \left( \frac{\rho u_r}{\rho} \right) + \frac{u_r}{r} \frac{\partial}{\partial r} \left( \frac{\rho u_r}{\rho} \right) + \frac{u_{\theta}}{r} \frac{\partial}{\partial \theta} \left( \frac{\rho u_r}{\rho} \right) + u_{\theta} \frac{\partial}{\partial z} \left( \frac{\rho u_r}{\rho} \right) =
-\varepsilon_t \frac{\partial \rho}{\partial z} + \mu_t \frac{\partial}{\partial z} \left( \frac{1}{r} \frac{\partial \rho}{\partial r} \right) \left( \frac{1}{r^2} \frac{\partial^2 \rho}{\partial \theta^2} \right) + \frac{1}{r^2} \frac{\partial^2 \rho}{\partial z^2} - \frac{2}{r^2} \frac{\partial \rho}{\partial \theta}. \tag{2}
\]

- Continuity and momentum balance equations for the viscous Newtonian and ideal gas phase,

\[
\frac{\partial}{\partial t} (\rho_g \varepsilon_g) + \frac{\partial}{\partial z} (\rho_g \varepsilon_g u_{z,g}) + \frac{1}{r} \frac{\partial}{\partial r} (r \rho_g \varepsilon_g u_{r,g}) + \frac{1}{r} \frac{\partial}{\partial \theta} (\rho_g \varepsilon_g u_{\theta,g}) = -\sum_{j} N_g M_j, \tag{5}
\]

\[
\frac{\partial}{\partial t} (\rho_g \varepsilon_g u_{z,g}) + u_{z,g} \frac{\partial}{\partial z} (\rho_g \varepsilon_g u_{z,g}) + \frac{u_{\theta}}{r} \frac{\partial}{\partial \theta} (\rho_g \varepsilon_g u_{z,g}) + u_{\theta} \frac{\partial}{\partial z} (\rho_g \varepsilon_g u_{z,g}) =
-\varepsilon_g \frac{\partial \rho_g}{\partial z} + \mu_g \frac{\partial}{\partial z} \left( \frac{1}{r} \frac{\partial \rho_g}{\partial r} \right) \left( \frac{1}{r^2} \frac{\partial^2 \rho_g}{\partial \theta^2} \right) + \frac{1}{r^2} \frac{\partial^2 \rho_g}{\partial z^2} - \frac{2}{r^2} \frac{\partial \rho_g}{\partial \theta}. \tag{6}
\]
quickly the equilibrium. The equilibrium of this reaction has been studied by Bodenstein [29] and the catalysts.

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The equilibrium constant is:

\[ K = \frac{p_{\text{NO}_2}^2}{p_{\text{NO}}^2} \]

mass transfer and the reaction in the liquid phase follow the sequence:

\[ \text{Liquid and gas phases and gas-liquid mass transfer} \ [5,27] \]

The main route of the absorption mechanism is extremely complex connecting reactions in both liquid and gas phases and gas-liquid mass transfer [5,27]. The main route of the absorption mechanism engages N\textsubscript{2}O\textsubscript{4} as the liquid phase reactant. The generation of N\textsubscript{2}O\textsubscript{4} in the gas phase, the gas-liquid mass transfer and the reaction in the liquid phase follow the sequence:

2.2. Mass and Energy Transport Model

2.2.1. Nitrogen Oxides Absorption Mechanism

The mechanism of nitrogen oxides absorption is extremely complex connecting reactions in both liquid and gas phases and gas-liquid mass transfer [5,27]. The main route of the absorption mechanism engages N\textsubscript{2}O\textsubscript{4} as the liquid phase reactant. The generation of N\textsubscript{2}O\textsubscript{4} in the gas phase, the gas-liquid mass transfer and the reaction in the liquid phase follow the sequence:

Reaction 1 : \( 2\text{NO}(g) + \text{O}_2 \rightarrow 2\text{NO}_2(g) \).

Reaction 2 : \( 2\text{NO}_2(g) \leftrightarrow \text{N}_2\text{O}_4(g) \).

Reaction 3 : \( \text{N}_2\text{O}_4(g) \leftrightarrow \text{N}_2\text{O}_4(\ell) \).

Reaction 4 : \( \text{N}_2\text{O}_4(\ell) + \text{H}_2\text{O}(\ell) \leftrightarrow \text{HNO}_3(\ell) + \text{HNO}_2(\ell) \).

Reaction 5 : \( 3\text{HNO}_2(\ell) \leftrightarrow \text{HNO}_3(\ell) + \text{H}_2\text{O}(\ell) + 2\text{NO}(g) \).

The equilibrium and kinetics of reaction 1 (NO gas phase oxidation) have been investigated by Bodenstein [28,29]. The oxidation rate expression is [27]:

\[ R_1' = k_1 p_{\text{NO}}^2 p_{\text{O}_2} - \frac{P_{\text{NO}_2}}{K_1}, \quad \text{[kPa/s]} \]

where \( k_1 = \exp(1468/T - 10.9043), \quad \text{[kPa}^{-2}\text{s}^{-1}] \),

\[ K_1 = \exp(-8.002 + 1.75\ln T - 0.000217T - 2496/T), \quad \text{[kPa]}. \]

NO gas phase oxidation reaction is the rate limiting step in the absorption process and is significantly influenced by the pressure [5,27]. \text{NO}_2 gas phase dimerization (Reaction 2) attains the equilibrium quickly. The equilibrium of this reaction has been studied by Bodenstein [29] and the equilibrium constant is:

\[ K_2 = \frac{P_{\text{NO}_2}}{p_{\text{NO}_2}} \quad K_2 = \exp(6893/T - 25.865), \quad \text{[kPa}^{-1}] \]
The liquid phase reactions 4 and 5 are often assembled into a global reaction with an effective rate that considers both the kinetic and transport process [5,27]:

\[
\frac{3}{2} N_2O_4(ℓ) + H_2O(ℓ) \leftrightarrow 2HNO_3(ℓ) + NO(g).
\] (19)

Dekker et al. [30] used the penetration theory to determine the rate of absorption of NO\textsubscript{2} in water considering the following assumptions: (a) NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{4} are in a permanent chemical equilibrium in the gas phase and are transferred from the bulk to the gas-liquid interface by molecular diffusion; (b) N\textsubscript{2}O\textsubscript{4} is the only species dissolved in H\textsubscript{2}O at the gas-liquid interface; (c) the liquid mass transfer of N\textsubscript{2}O\textsubscript{4} is accompanied by a rapid pseudo first-order reaction (H\textsubscript{2}O is in large excess). The N\textsubscript{2}O\textsubscript{4} absorption rate was stated as [30]:

\[
N_{N_2O_4} = H_{N_2O_4}P_{N_2O_4}\sqrt{k_{4,5}D_{N_2O_4}}.
\] (20)

2.2.2. SO\textsubscript{2} Absorption Mechanism

The major component of SO\textsubscript{x} emissions from ships engines is SO\textsubscript{2} [3]. When SO\textsubscript{2} is absorbed in pure water the ensuing reaction occurs in the liquid phase:

\[
SO_2 + H_2O \leftrightarrow H^+ + HSO_3^-.
\] (21)

The forward reaction rate constant was approximated to be very high (>10\textsuperscript{6} s\textsuperscript{-1}) at 293 K [31] and this reaction can be assumed to be an instantaneous reaction with respect to mass transfer [32]. The SO\textsubscript{2} absorption rate can be written as [32]:

\[
N_{SO_2} = k_{a}(C_{SO_2,i} - C_{SO_2,ℓ})E.
\] (22)

The absorption of SO\textsubscript{2} into seawater, which contains NaCl, can be considered a reversible reaction \(A(SO_2) \leftrightarrow B(HSO_3^-) + C(H^+)\) and the mass transfer enhancement factor was estimated, with the surface renewal model, as [32]:

\[
E = 1 + \frac{D_B C_{C,i} - C_{C,ℓ}}{D_A C_{A,i} - C_{A,ℓ}},
\] (23)

in which

\[
C_{C,i} = \frac{D_B}{D_C} C_{B,i} + \sqrt{\left(C_{C,i} - \frac{D_B}{D_C} C_{B,i}\right)^2 + 4 \frac{D_B}{D_C} C_{A,i} K_t}.
\] (24)

2.2.3. CO\textsubscript{2} Absorption Mechanism

Only the physical absorption in seawater was considered for CO\textsubscript{2} and the rate of absorption was given by Equation (22) with \(E = 1\).

2.2.4. Mass Conservative Equations

In the gas phase, only NO oxidation reaction was considered. The reaction between SO\textsubscript{2} and NO\textsubscript{x} was neglected and SO\textsubscript{2} was considered to be oxidized via the liquid phase routes, which is the slowest one [5]. SO\textsubscript{2} and NO\textsubscript{2} are absorbed separately in the liquid film and react independently with seawater (Ellison and Eckert 1984; Iloeje et al., 2015). The catalytic effect of NO\textsubscript{2} on aqueous phase SO\textsubscript{2} oxidation was neglected [5,33]. At high pressure, when gas phase NO oxidation rate is large [5], SO\textsubscript{2} and NO\textsubscript{x} simultaneous absorption in seawater is accompanied by very fast reactions in the liquid film neighboring the gas-liquid interface, and, consequently, the liquid bulk concentrations for SO\textsubscript{2} and NO\textsubscript{2} can be neglected. Therefore, the dynamic mass transport model includes the species balance equations for CO\textsubscript{2}, H\textsuperscript{+} and HSO\textsubscript{3}\textsuperscript{-} in the liquid phase and CO\textsubscript{2}, SO\textsubscript{2}, NO and NO\textsubscript{2} in the gas phase.
N$_2$O$_4$ concentration in the gas phase was evaluated via the equilibrium equation (Equation (18)). The unsteady-state 3-D species balance equations accounting for the non-uniform velocity profiles and the matching boundary conditions are:

- **Species balance equations in the gas phase**, 

\[
\frac{\partial}{\partial t}(\varepsilon_g P_{CO_2,g}) + u_{gr} \frac{\partial}{\partial r}(\varepsilon_g P_{CO_2,g}) + \frac{u_{gr}}{r} \frac{\partial}{\partial \theta}(\varepsilon_g P_{CO_2,g}) + u_{gr} \frac{\partial}{\partial z}(\varepsilon_g P_{CO_2,g}) = \\
D_{gr} \frac{\partial}{\partial r}(r \epsilon_g \frac{\partial}{\partial r}(\varepsilon_g P_{CO_2,g})) + \frac{D_{gr}}{r^2} \frac{\partial^2}{\partial \theta^2}(\varepsilon_g P_{CO_2,g}) + D_{gr} \frac{\partial^2}{\partial z^2}(\varepsilon_g P_{CO_2,g}) \\
- (N_{CO_2,g})RT_g
\]

\[
\frac{\partial}{\partial t}(\varepsilon_g P_{SO_2,g}) + u_{gr} \frac{\partial}{\partial r}(\varepsilon_g P_{SO_2,g}) + \frac{u_{gr}}{r} \frac{\partial}{\partial \theta}(\varepsilon_g P_{SO_2,g}) + u_{gr} \frac{\partial}{\partial z}(\varepsilon_g P_{SO_2,g}) = \\
D_{gr} \frac{\partial}{\partial r}(r \epsilon_g \frac{\partial}{\partial r}(\varepsilon_g P_{SO_2,g})) + \frac{D_{gr}}{r^2} \frac{\partial^2}{\partial \theta^2}(\varepsilon_g P_{SO_2,g}) + D_{gr} \frac{\partial^2}{\partial z^2}(\varepsilon_g P_{SO_2,g}) \\
- (N_{SO_2,g})RT_g
\]

\[
\frac{\partial}{\partial t}(\varepsilon_g P_{NO,g}) + u_{gr} \frac{\partial}{\partial r}(\varepsilon_g P_{NO,g}) + \frac{u_{gr}}{r} \frac{\partial}{\partial \theta}(\varepsilon_g P_{NO,g}) + u_{gr} \frac{\partial}{\partial z}(\varepsilon_g P_{NO,g}) = \\
D_{gr} \frac{\partial}{\partial r}(r \epsilon_g \frac{\partial}{\partial r}(\varepsilon_g P_{NO,g})) + \frac{D_{gr}}{r^2} \frac{\partial^2}{\partial \theta^2}(\varepsilon_g P_{NO,g}) + D_{gr} \frac{\partial^2}{\partial z^2}(\varepsilon_g P_{NO,g}) \\
- 2R_1(P_{lg})RT_g
\]

\[
\frac{\partial}{\partial t}(\varepsilon_g P_{NO_2,g}) + u_{gr} \frac{\partial}{\partial r}(\varepsilon_g P_{NO_2,g}) + \frac{u_{gr}}{r} \frac{\partial}{\partial \theta}(\varepsilon_g P_{NO_2,g}) + u_{gr} \frac{\partial}{\partial z}(\varepsilon_g P_{NO_2,g}) = \\
D_{gr} \frac{\partial}{\partial r}(r \epsilon_g \frac{\partial}{\partial r}(\varepsilon_g P_{NO_2,g})) + \frac{D_{gr}}{r^2} \frac{\partial^2}{\partial \theta^2}(\varepsilon_g P_{NO_2,g}) + D_{gr} \frac{\partial^2}{\partial z^2}(\varepsilon_g P_{NO_2,g}) \\
+ 2R_1(P_{lg})RT_g - 2(N_{N_2O_4,a})RT_g
\]

- **Species balance equations in the liquid phase**, 

\[
\frac{\partial}{\partial t}(\varepsilon_l C_{CO_2,l}) + u_{rl} \frac{\partial}{\partial r}(\varepsilon_l C_{CO_2,l}) + \frac{u_{rl}}{r} \frac{\partial}{\partial \theta}(\varepsilon_l C_{CO_2,l}) + u_{rl} \frac{\partial}{\partial z}(\varepsilon_l C_{CO_2,l}) = \\
D_{rl} \frac{\partial}{\partial r}(r \epsilon_l \frac{\partial}{\partial r}(\varepsilon_l C_{CO_2,l})) + D_{rl} \frac{\partial^2}{\partial \theta^2}(\varepsilon_l C_{CO_2,l}) + D_{rl} \frac{\partial^2}{\partial z^2}(\varepsilon_l C_{CO_2,l}) \\
+ N_{CO_2,a}
\]

\[
\frac{\partial}{\partial t}(\varepsilon_l C_{H^+,l}) + u_{rl} \frac{\partial}{\partial r}(\varepsilon_l C_{H^+,l}) + \frac{u_{rl}}{r} \frac{\partial}{\partial \theta}(\varepsilon_l C_{H^+,l}) + u_{rl} \frac{\partial}{\partial z}(\varepsilon_l C_{H^+,l}) = \\
D_{rl} \frac{\partial}{\partial r}(r \epsilon_l \frac{\partial}{\partial r}(\varepsilon_l C_{H^+,l})) + D_{rl} \frac{\partial^2}{\partial \theta^2}(\varepsilon_l C_{H^+,l}) + D_{rl} \frac{\partial^2}{\partial z^2}(\varepsilon_l C_{H^+,l}) \\
+ N_{SO_2,a}
\]

\[
\frac{\partial}{\partial t}(\varepsilon_l C_{HSO_3^-,l}) + u_{rl} \frac{\partial}{\partial r}(\varepsilon_l C_{HSO_3^-,l}) + \frac{u_{rl}}{r} \frac{\partial}{\partial \theta}(\varepsilon_l C_{HSO_3^-,l}) + u_{rl} \frac{\partial}{\partial z}(\varepsilon_l C_{HSO_3^-,l}) = \\
D_{rl} \frac{\partial}{\partial r}(r \epsilon_l \frac{\partial}{\partial r}(\varepsilon_l C_{HSO_3^-,l})) + D_{rl} \frac{\partial^2}{\partial \theta^2}(\varepsilon_l C_{HSO_3^-,l}) + D_{rl} \frac{\partial^2}{\partial z^2}(\varepsilon_l C_{HSO_3^-,l}) \\
+ N_{SO_2,a}
\]

\[
z = 0 \quad u_{rl} \varepsilon_l C_{H^+,l}|_{z=0} = 0 - \varepsilon_l D_{rl} \frac{\partial C_{H^+,l}}{\partial z} \bigg|_{z=0} = 0,
\]

\[
z = 0 \quad u_{rl} \varepsilon_l C_{HSO_3^-,l}|_{z=0} = 0 - \varepsilon_l D_{rl} \frac{\partial C_{HSO_3^-,l}}{\partial z} \bigg|_{z=0} = 0.
\]
2.3. Model Parameters

Convection, conduction in radial and azimuthal directions, gas-liquid heat transfer and absorption reaction heats were included in the energy balance equations for gas and liquid phases. The interfacial temperature was evaluated via the continuity of the energy flux throughout the gas-liquid interface [34]. The heat of CO\textsubscript{2} physical absorption and the heat losses were neglected.

- **Heat balance equations in liquid and gas phase,**

\[
\left( \rho \varepsilon C_{pL} \frac{\partial T_{\ell}}{\partial t} + \rho \varepsilon C_{pL} \frac{\partial T_{\ell}}{\partial r} \right) r + \rho \varepsilon C_{pL} \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r} \right) T_{\ell} + \rho \varepsilon C_{pL} \frac{\partial}{\partial \theta} \left( \frac{1}{r} \frac{\partial}{\partial r} \right) T_{\ell} = \frac{\lambda_{f,\ell}}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T_{\ell}}{\partial r} \right),
\]

\[
+ \frac{\lambda_{f,\ell}}{r^2} \frac{\partial^2 T_{\ell}}{\partial \theta^2} + \left( -\Delta H_{r,N_2O_4} \right) N_{N_2O_4} a + \left( -\Delta H_{r,SO_2} \right) N_{SO_2} a - \alpha_{g,\ell} a (T_{\ell} - T_i) \]

\[
+ \frac{\lambda_{f,\ell}}{r^4} \frac{\partial^3 T_{\ell}}{\partial \theta^3}, (38)
\]

- **Heat balance at the gas-liquid interface,**

\[
- \sum_{j} N_{j}^{\text{trans}} a H_{j}^{S} + \sum_{j} \hat{N}_{j}^{\text{trans}} a H_{j}^{L} = \alpha_{g,\ell} a (T_{\ell} - T_i) - \alpha_{g,\ell} a (T_i - T_g).
\]

The boundary conditions are:

\[
z = 0 \quad T_{\ell|z=0} = T_{\ell|z} = 0,
\]

\[
z = H \quad \frac{\partial T_{\ell}}{\partial z} = 0 \quad T_{\ell|z=H} = T_{\ell|z} = 0,
\]

\[
r = 0 \quad \frac{\partial T_{\ell|z}}{\partial r} = 0,
\]

\[
r = R \quad \frac{\partial T_{\ell|z}}{\partial r} = 0,
\]

\[
\theta = 0, 2\pi \quad \frac{\partial T_{\ell|z}}{\partial \theta} = 0.
\]

2.2.5. Energy Balance Equations

The boundary conditions are:

\[
z = 0 \quad u_{g} \varepsilon g \rho_{g} P_{g|z} = u_{g} \varepsilon g \rho_{g} P_{g|z} \bigg|_{z=H} = \varepsilon g D_{g} \frac{\partial P_{g|z}}{\partial z} \bigg|_{z=H},
\]

\[
r = 0 \quad \frac{\partial C_{f,\ell}}{\partial r} = 0 \quad \frac{\partial P_{g|z}}{\partial r} = 0,
\]

\[
r = R \quad \frac{\partial C_{f,\ell}}{\partial r} = 0 \quad \frac{\partial P_{g|z}}{\partial r} = 0,
\]

\[
\theta = 0, 2\pi \quad \frac{\partial C_{f,\ell}}{\partial \theta} = 0 \quad \frac{\partial P_{g|z}}{\partial \theta} = 0.
\]
viscosities ($\mu_{eff}^{f}$), integrating viscous and pseudo-turbulence stress tensors, were formulated as suggested by Dankworth et al. [35]. H$^+$ and HSO$_3^-$ molecular diffusion coefficients in seawater were taken from Hikita et al. [36] and Chang and Rochelle [32]. The additional molecular diffusion coefficients were estimated via the Wilke-Chang method (in Poling et al. [37]). Solubilities of gaseous components in seawater were evaluated using the gas-liquid equal-fugacity conditions proposed by Rodriguez-Sevilla et al. [38]:

$$m_j = \frac{P_j \Phi_j}{H_j \gamma_j^0}.$$

(45)

CO$_2$ and SO$_2$ Henry’s constant correlations in water were taken from Plummer and Busenberg [39] and Rodriguez-Sevilla et al. [40]. The activity coefficients in seawater have been evaluated with the correlation suggested by Schumpe [41]:

$$\log \gamma_j = \sum_i \left(h_{i,j} + h_j\right)C_i,$$

(46)

$h_{i,j}$ is the specific parameter of the ion $i$, $h_j$ is the gas specific parameter, and $C_i$ is the molar concentration of the ion $i$. $h_{i,j}$ and $h_{SO_2}$ were obtained from Schumpe [41], Weisenberger and Schumpe [42] and Rodriguez-Sevilla et al. [38] and $h_{CO_2}$ and $h_{N_2O_4}$ were taken from Chang and Rochelle [32] and Armor [43].

Effective thermal conductivities were calculated with the relationship of Weekman and Myers [44] and seawater thermal conductivity was evaluated with Filippov equation and Sastri method (in Poling et al., [37]). Chilton-Colburn heat/mass transfer analogy was applied to calculate the interfacial conductive heat transfer coefficient (Taylor and Krishna, [34]). Gas-liquid mass transfer parameters (gas-liquid interfacial area and gas-liquid mass transfer coefficients) at the local level were evaluated via the macroscopic mass transfer correlations of Onda et al. [45] quantified as a function of local liquid velocity. Liquid and gas dispersion coefficients in the axial direction were acquired from Sater and Levenspiel [46] and Otake and Kunugita [47] and the ratio between the axial and azimuthal/radial dispersion coefficients was presumed to be 10 [48].

2.4. Numerical Implementation

The partial differential equations which define the dynamics of gas-liquid countercurrent flow and simultaneous absorption of SO$_2$, NO$_x$ and CO$_2$ in vertical, inclined and oscillating/heaving countercurrent packed-bed column reactors were resolved in Aspen Custom Modeler. The discretization of the model equations in the three spatial directions was realized via the second and third order orthogonal collocation on finite elements technique. Newton and Gear integration procedures were implemented to resolve steady-state and unsteady-state models.

3. Results and Discussion

3.1. Model Experimental Validation

Figure 2 shows a comparison between theoretical and experimental SO$_2$ absorption data obtained by Flagiello et al. [9] via a seawater scrubbing process in a structured packed-bed column ($D = 0.1$ m; $H = 0.892$ m) with Sulzer Mellapak 250X. Theoretical SO$_2$ removal efficiency matches the experimental SO$_2$ removal efficiency generated at different gas and liquid flow rates and SO$_2$ concentrations in the gas phase.
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Figure 2. Experimental and theoretical SO$_2$ removal efficiency in a seawater structured packed-bed column packed with Sulzer Mellapak 250X (D = 0.1 m; H = 0.892 m). Experimental data were taken from Flagiello et al. [9].

Figures 3 and 4 illustrate the theoretical and experimental CO$_2$ chemical absorption data obtained by Tontiwachwuthikul et al. [49] via a CO$_2$-MEA absorption process in a random packed-bed column reactor with 12.7 mm ceramic Berl saddles (D = 0.1 m; H = 6.55 m). Simulated CO$_2$ absorption results are acceptably close to the experimental data performed at various monoethanolamine (MEA)/CO$_2$ concentrations in the liquid/gas phase and different values for gas and liquid flow rates. However, these conditions are different from the ones simulated with the current model (absorption in seawater and not amine solutions). Simulations of the CO$_2$-MEA absorption process behavior in vertical, static inclined, and dynamic inclined countercurrent random packed-bed columns were presented in Iliuta and Larachi [26].

Figure 3. Cont.
In addition, the enzymatic CO$_2$ removal experimental data generated by Rambo et al. [50] in a structured packed-bed column (D = 0.05 m; H = 1.06 m) with immobilized human carbonic anhydrase II (hCA II) on Sulzer Mellapak 500X were compared with the predictions of a similar dynamic 3-D model which associates the macroscopic momentum and mass balance equations in the gas and liquid phases with concomitant diffusion and reaction within the hCA II enzyme washcoat [22]. Table 1 shows that theoretical enzymatic CO$_2$ removal results suit the experimental data generated at different hCA II loadings.
3.2. Removal Performance in Vertical and Inclined Packed-Bed Columns

In vertical packed-bed columns, under similar operating conditions (Table 2), the comparable preloading hydrodynamics (not shown) generates a similar NO\textsubscript{x}, SO\textsubscript{2} and CO\textsubscript{2} removal efficiency when working with third generation (I-Rings) and fourth generation (Raschig super-Rings No. 0.3) packings (Figures 5 and 6). The removal performance of packed-bed column with Pall-Rings exceeds marginally the removal performance of scrubbers filled with I-Rings and Raschig super-Rings, due to the larger specific surface area of the packings. However, the modern random packings give much smaller two-phase pressure drop than Pall-Rings (Figure 7), while maintaining comparable removal efficiency (Figures 5 and 6). The similar hydrodynamics of packed-bed column reactors with third and fourth generation packings results from comparable bed porosity and packing specific area (Table 2). With the increase of scrubber pressure, the NO\textsubscript{x} removal process is improved because of the increased reaction rate of NO gas phase oxidation which is rate-limiting in the absorption process. The impact of pressure on SO\textsubscript{2} removal is even more significant and, at large pressure, SO\textsubscript{2} is totally removed in the entrance region of the scrubber. SO\textsubscript{2} removal is completely in the entire range of scrubber pressure and when the pressure increases SO\textsubscript{2} is removed more quickly. Working with large pressure and large packed bed heights speed up the rate limiting pressure dependent NO oxidation reaction leading to a large NO\textsubscript{x} removal efficiency. Moreover, the physical absorption of CO\textsubscript{2} in seawater is significantly amplified at high pressure. However, even if the seawater scrubbing at elevated pressure increases the capital cost and the energy requirement we implemented this approach for offshore conditions because of: (i) Simultaneous cut of SO\textsubscript{2} and NO\textsubscript{x} from exhaust gas; (ii) 100% removal of SO\textsubscript{2} although the sulfur concentration in the fuel is larger than 3.5%; (iii) avoidance of the losing of engine power because of the large counter pressure to the incoming exhaust (which takes place in scrubbers operated at atmospheric pressure because of the pressure drop in the packed-bed column). Additional advantages are given in Section 1.

<table>
<thead>
<tr>
<th>Enzyme Loading (g/\text{L}_{\text{reactor}})</th>
<th>CO\textsubscript{2} Conversion Experimental</th>
<th>CO\textsubscript{2} ConversionModel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.898</td>
<td>0.74</td>
<td>0.752</td>
</tr>
<tr>
<td>2.301</td>
<td>0.73</td>
<td>0.7525</td>
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<tr>
<td>4.931</td>
<td>0.73</td>
<td>0.753</td>
</tr>
<tr>
<td>5.003</td>
<td>0.72</td>
<td>0.7533</td>
</tr>
<tr>
<td>5.699</td>
<td>0.68</td>
<td>0.753</td>
</tr>
<tr>
<td>6.147</td>
<td>0.72</td>
<td>0.753</td>
</tr>
</tbody>
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Figure 5. SO$_2$ and NO removal efficiency vs. scrubber pressure (H = 5 m): (a) Packed-bed column with Raschig super-Rings; (b) Packed-bed column with I-Rings; (c) Packed-bed column with Pall-Rings.

Figure 6. Cont.
Figure 6. Steady-state axial profiles of liquid phase CO$_2$ concentration at different values of scrubber pressure ($H = 5$ m): (a) Packed-bed column with Raschig super-Rings; (b) Packed-bed column with I-Rings; (c) Packed-bed column with Pall-Rings.

Figure 7. Steady-state axial profiles of gas-phase dimensionless pressure in random packed-bed columns (Base case operating conditions—Table 2; $P = 2.5$ MPa; $H = 5$ m).
NOx removal efficiency declines at larger packed-bed column inclinations (Figures 8 and 9), even if the local N2O4 absorption process improves in the lowermost area located in the neighborhood of the wall on the slanted side of the scrubber. The higher scrubber pressure pulls up NO oxidation reaction yielding additional NO2 for absorption, especially in the lowermost area. This averts large deficits in NOx removal at large scrubber inclinations. In the case of packed-bed columns with considerable height, the rate of production of NO2 from NO is balanced by the rate of consumption via N2O4 absorption in seawater in the entire range of scrubber inclination (Figure 9). However, NOx removal efficiency is not downgraded significantly by the inclination of packed-bed column, as in the case of other removal processes [22, 24, 26], because of the large operational pressure and because the diffusion of N2O4 into the liquid phase is associated with a rapid pseudo first-order reaction between N2O4 and a large excess of water. CO2 physical absorption efficiency is lowered at larger packed-bed column inclinations (Figure 10) although the local physical absorption process expands in the lowermost area. As in the case of NOx removal, the higher scrubber pressure reduces the deficit in CO2 removal at large packed-bed column inclinations. Thus, the pressure is a key design parameter which affects the operation of the scrubber column and the removal of both NOx and CO2 under vertical and inclined conditions. SO2 is removed quickly (verifying the assumption of no reaction between SO2 and NO2 in the gas phase) and the removal efficiency is not reduced by the inclination of packed-bed column (Figure 11) because the absorption is an instantaneous reversible reaction with respect to mass transfer (enhancement factor between 6 and 10) and the absorption rate is entirely limited by reactants diffusion. The simulations were carried out in inclined packed-bed columns with fourth generation Raschig super-Rings under the operating conditions listed in Table 2 (the gas composition emulates typical emissions of marine diesel engines: Nielsen et al. [1]; Yang et al. [6]; Tang et al. [14]).

![Figure 8. NO and SO2 removal efficiency vs. seawater scrubber inclination angle (Packed-bed column with Raschig super-Rings).](image-url)
Figure 9. Steady-state axial profiles of NO$_2$ partial pressure at different values of seawater scrubber inclination angle (Packed-bed column with Raschig super-Rings): (a) $H = 5$ m; $P = 1.5$ MPa; (b) $H = 8$ m; $P = 2.5$ MPa.

Figure 10. CO$_2$ removal efficiency vs. seawater scrubber inclination angle (packed-bed column with Raschig super-Rings): (a) $H = 5$ m; (b) $H = 8$ m.
**Figure 10.** CO$_2$ removal efficiency vs. seawater scrubber inclination angle (packed-bed column with Raschig super-Rings): (a) H = 5 m; (b) H = 8 m.

**Figure 11.** Steady-state axial profiles of SO$_2$ partial pressure at different values of scrubber pressure (Packed-bed column with Raschig super-Rings, Packed-bed column inclination angle = 15 deg): (a) H = 5 m; (b) H = 8 m.
The downgrading of NO\textsubscript{x} and CO\textsubscript{2} removal performance at scrubber inclination is linked to the loss of axial symmetry of two-phase flow in the radial direction (e.g., Figure 12 for liquid holdup and axial velocity) which leads to an asymmetric gas-liquid mass transfer because of asymmetric gas-liquid interfacial areas (Figure 13), and asymmetric temperature and scrubber performance (Figure 14). Such setbacks are the result of secondary liquid flows induced by the gravity-forced movement of liquid towards the lowermost area [17,24]. This tendency is slightly amplified by the higher temperature (mainly in the area with considerable NO, SO\textsubscript{2} and CO\textsubscript{2} gas phase concentration) initiated in the uppermost side of the scrubber (Figure 14), where liquid flow decelerated occasioning weakening of the local NO\textsubscript{x} and CO\textsubscript{2} removals. Another factor at the decrease of NO\textsubscript{x} and CO\textsubscript{2} absorption efficiency at larger scrubber inclinations is linked to the deterioration of gas-liquid mass transfer in the uppermost zone which is partially caught up by the improved NO\textsubscript{x} and CO\textsubscript{2} removal in the lowermost zone. However, the reduction of NO\textsubscript{x} and CO\textsubscript{2} absorption performance at large inclinations can be contained by rising the scrubber pressure.

\begin{table}[h]
\centering
\caption{Parameters used in simulations.}
\begin{tabular}{ll}
\hline
\textbf{Operating Conditions} & \textbf{Data} \\
\hline
Scrubber height & 5.0 and 8 m \\
Scrubber diameter & 0.43 m \\
Packing specific area (Raschig super-Rings No. 0.3)/Bed porosity & 315 m\textsuperscript{2}/m\textsuperscript{3}/0.96 \\
Packing specific area (I-Rings)/Bed porosity & 305 m\textsuperscript{2}/m\textsuperscript{3}/0.97 \\
Packing specific area (Pall-Rings)/Bed porosity & 360 m\textsuperscript{2}/m\textsuperscript{3}/0.92 \\
Scrubber pressure & 0.1–3 MPa \\
Scrubber inlet temperature & 298 K \\
Superficial gas velocity & 0.4 m/s \\
Superficial liquid velocity & 0.015 m/s \\
Inlet gas composition (mole fraction): & - \\
SO\textsubscript{2} & 0.002 \\
NO & 0.0015 \\
NO\textsubscript{2} & 0.00015 \\
CO\textsubscript{2} & 0.05 \\
O\textsubscript{2} & 0.15 \\
The ionic composition of seawater, mol/L & - \\
Cl\textsuperscript{-} & 0.56 \\
Na\textsuperscript{+} & 0.5 \\
SO\textsubscript{4}\textsuperscript{2-} & 0.03 \\
HCO\textsubscript{3}\textsuperscript{-} & 0.003 \\
Seawater salinity & 36.87 g/kg \\
Seawater ionic strength & 0.775 mol/kg \\
Spreading factor & 0.0074 \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.png}
\caption{Cont.}
\end{figure}
**Figure 12.** Steady-state radial profiles of axial liquid velocity in x-axis (see Figure 1)—vertical and inclined seawater scrubbers (Packed-bed column with Raschig super-Rings; H = 5 m; z/H = 0.8): (a) Pressure = 1.5 MPa; (b) Pressure = 2.5 MPa.

**Figure 13.** Steady-state radial profiles of gas-liquid interfacial area in x-axis (see Figure 1)—vertical and inclined seawater scrubbers (Packed-bed column with Raschig super-Rings; H = 5 m; z/H = 0.8): (a) Pressure = 1.5 MPa; (b) Pressure = 2.5 MPa.
Figure 14. Steady-state radial profiles of liquid temperature (a) and NO partial pressure (b) in x-axis (see Figure 1)—vertical and inclined seawater scrubbers (Packed-bed column with Raschig super-Rings; $H = 5$ m; $z/H = 0.8$; Pressure $= 2.5$ MPa).

Rise of liquid flow rate in the vertical position improves NO$_x$ and CO$_2$ removal performance. Contrarily, at considerable scrubber inclinations the underperformance of NO$_x$ and CO$_2$ removal process becomes higher with the increase of liquid velocity (Figure 15) and follows the considerable shift of axial symmetry of two-phase flow in the radial direction (illustrated in Figure 16a,b for liquid axial velocity and in Figure 16c,d for liquid holdup). The reason of this atypical behavior is the high complexity of the mechanism of nitrogen oxides absorption involving reactions in both liquid and gas (NO oxidation reaction: Limiting step in the absorption process) phases and gas-liquid mass transfer. Also, the significant decline of the liquid holdup and velocity in the uppermost area (Figure 16) is related with the reinforcement of the gas-liquid mass transfer resistance which downgrades considerably the local N$_2$O$_4$ and CO$_2$ absorption processes (the increase of the gas phase residence time does not affect significantly NO$_x$ and CO$_2$ removal). Additionally, NO oxidation reaction and physical CO$_2$ absorption are negatively affected by the amplification of temperature in the uppermost area (Figure 14a) which induces the reduction of gas solubility in the liquid phase. For comparison, in inclined packed-bed columns for simultaneous absorption of CO$_2$ and H$_2$S in MEA the underperformance of the absorption process at considerable packed bed inclinations can be contracted by increasing the liquid velocity [26].
Figure 15. NO (a) and CO₂ (b) removal efficiency vs. seawater scrubber inclination angle at different values of liquid velocity (Packed-bed column with Raschig super-Rings; H = 5 m; Pressure = 2.5 MPa).
Figure 16. Steady-state radial profiles of cross-sectionally averaged liquid axial velocity (a,b) and liquid holdup (c,d) in x-axis (see Figure 1)—vertical and inclined seawater scrubbers (Packed-bed column with Raschig super-Rings; H = 5 m; z/H = 0.8; Pressure = 2.5 MPa): (a,c) Liquid superficial velocity = 0.035 m/s; (b,d) Liquid superficial velocity = 0.015 m/s.

3.3. Removal Performance in Packed-Bed Column under Heaving Motion Conditions

Submitted to a heaving motion (Figure 1iii), the column feels heaving acceleration added to the gravitational acceleration. A sinewave function was used to reproduce the heaving acceleration as a function of time [26].

The impact of heaving on scrubber hydrodynamics and NOx and CO2 removal performance is illustrated in Figures 17–20. The heaving acceleration amplitudes were programmed to be 1.5 and 2 m/s² [51] with heaving periods of 10 and 20 s. Heaving generates disturbance waves in two-phase countercurrent flow (illustrated for two-phase pressure drop and liquid axial velocity in Figures 17 and 19) around the steady-state solutions of the vertical scrubber static condition preceding the heaving motion with the wave height which expands at large heaving acceleration amplitude (Figure 17) and with longer wavelength at large heaving motion periods (Figure 19). As soon as seawater scrubber moves up, liquid axial velocity decreases and becomes smaller than its value in the static state preceding the heaving motion. Subsequently, the local relative velocity between the two fluids decreases and generates lower local interphase momentum exchange rates followed by a lower pressure drop. On the contrary, when seawater scrubber moves down the local liquid axial velocity and two-phase pressure drop increase and becomes higher than their values in the vertical scrubber static state. The waves in two-phase countercurrent flow have the crest and trough when the heaving acceleration comes close to the maximum (scrubber in bottom position) or minimum (scrubber in top position).
Figure 17. Time-dependent cross-sectionally averaged axial liquid velocity (a) and two-phase pressure drop (b) in a seawater scrubber under heaving motion conditions at different heaving acceleration amplitudes (Packed-bed column with Raschig super-Rings; $H = 5$ m; Pressure = 1.5 MPa).
Figure 18. Time-dependent exit NO (a) and CO$_2$ (b) partial pressure in a seawater scrubber under heaving motion conditions at different heaving acceleration amplitudes (Packed-bed column with Raschig super-Rings; $H = 5$ m; Pressure = 1.5 MPa).
**Figure 19.** Time-dependent cross-sectionally averaged axial liquid velocity (a) and two-phase pressure drop (b) in a seawater scrubber under heaving motion conditions at different heaving motion periods (Packed-bed column with Raschig super-Rings; H = 5 m; Pressure = 1.5 MPa).
Figure 20. Time-dependent exit NO (a) and CO$_2$ (b) partial pressure in a seawater scrubber under heaving motion conditions at different heaving motion periods (Packed-bed column with Raschig super-Rings; H = 5 m; Pressure = 1.5 MPa).

The impact of heaving is more notable on NO$_x$ and CO$_2$ removal performance because SO$_2$ absorption is an instantaneous reaction with respect to mass transfer. Similarly, the oscillatory seawater scrubber NO$_x$ and CO$_2$ removal performance, generated by oscillatory two-phase flow and gas-liquid mass transfer, is a function of the heaving acceleration (Figures 18 and 20). NO and CO$_2$ concentration waves, whose heights follow the extent of heaving acceleration amplitude (Figure 18), vary around the
steady-state solution of the scrubber static state preceding the heaving motion. NO and CO$_2$ partial pressure waves attain the crest and trough when the heaving acceleration comes close to minimum (scrubber in top position) or maximum (scrubber in bottom position); these seawater scrubber positions match the trough and crest of two-phase countercurrent flow waves.

Also, the oscillatory seawater scrubber removal performance is shaped by the magnitude of the heaving motion period (Figure 20). Time-dependent waves with longer wavelength are noticed at large heaving motion periods because of the amplification of oscillatory two-phase flow. The fluctuation periods of the waves are similar to the heaving motion period (after a transitional time in the case of two-phase pressure drop).

### 3.4. Removal Performance in Asymmetric/Symmetric Oscillating Packed-Bed Column

Under the episode of oscillation motion (Figure 1-iv, v, vi), the scrubber moves between vertical and an inclined position or between two asymmetrical/symmetrical inclined positions with a sinusoidal angular velocity [52].

Asymmetric oscillating scrubbers underperform with respect to the vertical configuration (Figure 21). The systematic cyclic variations of the extent of reverse secondary liquid flow, attributable to radial and azimuthal buoyancy force, inducts oscillatory two-phase flow (Figure 22) leading to oscillatory scrubber performances (Figure 21). Under the episode of asymmetric (vertical-inclined position move) oscillation, NO and CO$_2$ partial pressure time-dependent waves evolve not far from the steady-state solution of the median inclination angle (Figure 22) and mirror in magnitude the asymmetry of two-phase flow. The absorption performance waves move toward a steady-state solution of vertical scrubber when the asymmetry of the two inclined positions of the scrubber downgrades (not shown). However, the removal efficiency of SO$_2$ absorption remains unaffected under asymmetric externally-induced periodic oscillations.

![Figure 21. Cont.](image-url)
Figure 21. Time-dependent exit NO (a) and CO$_2$ (b) partial pressure in a seawater scrubber under angular sinusoidal oscillatory motion between the vertical and an inclined ($15^\circ$) position (Packed-bed column with Raschig super-Rings; H = 5 m; Pressure = 1.5 MPa; Travel time between the vertical/inclined and inclined/vertical positions = 10 s).

Figure 22. Cont.
Two-phase countercurrent flow and absorption efficiency in symmetric oscillating packed-bed columns have been simulated for other reaction cases [24]. Their trends were found transposable to the present reaction case for simultaneous NO\textsubscript{x}, SO\textsubscript{2} and CO\textsubscript{2} absorption in seawater with the exception of SO\textsubscript{2} absorption efficiency which keeps unaltered as for asymmetrical oscillatory motion. Symmetric oscillatory motion reflects in NO\textsubscript{x} and CO\textsubscript{2} removal performance disturbance waves around the steady-state vertical column solution with an extent determined by the angular motion parameters.

4. Conclusions

Simultaneous removal of NO\textsubscript{x} and SO\textsubscript{2} emissions from large marine diesel engines by seawater scrubbing was studied in countercurrent random packed-bed columns exposed to static inclination and heaving/oscillating motion via a 3-D dynamic model.

Simulation of seawater scrubber with fourth generation random packing (Raschig super-Rings) predicts smaller two-phase pressure drop in comparison with traditional Pall-Rings while maintaining comparable removal efficiency for the pollutants. Working at elevated pressure promotes the rate limiting NO oxidation reaction leading to a large NO\textsubscript{x} removal efficiency. Moreover, the physical absorption of CO\textsubscript{2} is improved significantly at high pressure.

SO\textsubscript{2} is absorbed quickly and the removal efficiency is not lowered by the inclination of seawater scrubber. In contrast, NO\textsubscript{x} and CO\textsubscript{2} removal efficiency are both negatively impacted at large packed-bed column inclinations even if the local N\textsubscript{2}O\textsubscript{4} and CO\textsubscript{2} absorption processes improve close to the wall region on the inclined side of the scrubber. The decay of NO\textsubscript{x} and CO\textsubscript{2} removal performance at large scrubber inclinations is reduced rising the pressure promoting gas-phase NO oxidation and yielding additional N\textsubscript{2}O\textsubscript{4} for absorption, especially in the lowermost area. Nevertheless, NO\textsubscript{x} removal efficiency is not significantly lowered by the scrubber inclination, unlike previously analyzed reaction cases, because of the larger pressure and because liquid diffusion of N\textsubscript{2}O\textsubscript{4} is accompanied by a rapid pseudo first-order reaction.

Heaving motion produces oscillatory patterns for NO\textsubscript{x} and CO\textsubscript{2} removal performance around the steady-state solution of the stationary scrubber. Exit NO and CO\textsubscript{2} partial pressure waves attain the
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crest/through when the heaving acceleration comes close to the minimum/maximum values (scrubber in top/bottom position), and this matches the trough/crest of two-phase countercurrent flow waves. The oscillatory seawater scrubber removal performance is a function of the heaving acceleration.

Asymmetric oscillating motion (vertical-inclined position move) deteriorates the removal performance which evolves by means of waves not far from the steady-state solution of the middle inclination angle. NO and CO2 absorption performance waves are moving toward a steady-state solution of vertical scrubber when the asymmetry of the two inclined positions of the scrubber downgrades. Symmetric oscillation gives performance disturbance waves around the steady-state solution of the vertical seawater scrubber which is fashioned by the parameters of angular motion.

Author Contributions: Conceptualization, I.I. and F.L.; Methodology, I.I.; Software, I.I.; Validation, I.I.; Formal Analysis, I.I.; Investigation, I.I.; Resources, I.I. and F.L.; Data Curation, I.I.; Writing-Original Draft Preparation, I.I.; Visualization, I.I.; Supervision, F.L.; Project Administration, F.L.; Funding Acquisition, F.L.

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Conflicts of Interest: The authors declare no conflict of interest.

Notation

\( a \) gas-liquid interfacial area, \( \text{m}^2/\text{m}^3 \)

\( a_h \) acceleration of heaving, \( \text{m/s}^2 \)

\( a_0 \) heaving acceleration amplitude, \( \text{m/s}^2 \)

\( a_s \) packing specific surface area (surface packing area/column volume), \( \text{m}^2/\text{m}^3 \)

\( c_{p,a} \) specific heat capacity of \( \alpha \)-phase (\( \alpha = g, l \)), \( \text{kJ/kgK} \)

\( C_j \) concentration of species \( j \), \( \text{kmol/m}^3 \)

\( d_p \) effective particle diameter, \( \text{m} \)

\( D \) column diameter, \( \text{m} \)

\( D_{gl} \) molecular diffusivity coefficient of species \( j \) in the liquid phase, \( \text{m}^2/\text{s} \)

\( D_{l(g)} \) liquid and gas dispersion coefficients, \( \text{m}^2/\text{s} \)

\( E \) mass transfer enhancement factor

\( E_{1}, E_{2} \) Ergun constants

\( f_e \) wetted fraction of the packing area

\( f_{\text{int},g} \) interaction force exerted on gas phase, \( \text{N/m}^3 \), \( f_{\text{int},g}(r,z) = f_e F_{g,z}(r,z) + (1 - f_e) F_{g,z}(r,z) \)

\( f_{\text{int},l} \) interaction force exerted on liquid phase, \( \text{N/m}^3 \), \( f_{\text{int},l}(r,z) = -\frac{e_f - e_l}{e_f} f_e F_{g,z}(r,z) + \frac{f_e f_{g,z}(r,z)}{(1 - f_e) F_{g,z}(r,z)} - f_e F_{l,z}(r,z) \)

\( F_{d,g} \) mechanical dispersion force in gas, \( \text{N/m}^3 \), \( F_{d,g}(r,z) = (1 - f_e) K_{g} u_{g,z}(r,z) + e_f f_{g} K_{g}(u_{g,z}(r,z) - u_{l,z}(r,z)) \)

\( F_{d,l} \) mechanical dispersion force in liquid, \( \text{N/m}^3 \), \( F_{d,l}(r,z) = f_e K_{l}(u_{l,z}(r,z)) - e_f K_{l}(u_{l,z}(r,z) - u_{g,z}(r,z)) \)

\( F_{g,z} \) gas-liquid drag force, \( \text{N/m}^3 \), \( F_{g,z}(r,z) = \left( \frac{E_1}{36} \frac{a_s^2 H_{g,2}}{e^2} + \frac{E_2}{6} a_s^3 \frac{\rho_g}{\rho_{g-f}} \sqrt{\frac{r_z^2 + r_r^2 + r_{l,0}^2}{2}} \left( \frac{r_z}{r_f} + \frac{r_r}{r_f} + \frac{r_{l,0}}{r_f} \right) \right) u_{g,z}(r,z) e_f \)

\( F_{g,s} \) gas-solid drag force, \( \text{N/m}^3 \), \( F_{g,s}(r,z) = \left( \frac{E_1}{36} \frac{a_s^2 H_{g,2}}{e^2} + \frac{E_2}{6} a_s^3 \rho_g \sqrt{\frac{u_{g,z}^2 + u_{g,s}^2 + u_{g,f}^2}{2}} \right) u_{g,z}(r,z) e_f \)

\( F_{l,s} \) liquid-solid drag force, \( \text{N/m}^3 \), \( F_{l,s}(r,z) = \left( \frac{E_1}{36} \frac{a_s^2 H_{g,2}}{e^2} + \frac{E_2}{6} a_s^3 \rho_f \sqrt{\frac{u_{l,z}^2 + u_{l,s}^2 + u_{l,f}^2}{2}} \right) u_{l,z}(r,z) e_f \)
gravitational acceleration, m/s²

scrubber height, m

molar enthalpy of species \( j \) in \( \alpha \)-phase, kJ/kmol

Henry’s law constant in molal unit

pseudo first-order reaction rate constant for \( \text{N}_2\text{O}_4 \) hydrolysis (Reaction 19), s⁻¹

gas phase mass transfer coefficient, m/s

volumetric liquid phase mass transfer coefficient, 1/s

effective equilibrium constant of the SO₂ absorption reaction, mol/L

molar concentration of component \( j \), kmol/kg, \( \sum C_j = \frac{m_j\rho_l}{1 + m_j M_{\text{H}_2\text{O}}} \)

molecular mass of component \( j \), kg/kmol

interfacial molar flux of component \( j \), kmol/m²s, \( \frac{N_j}{\alpha} = -D_j\ell \frac{\partial C_j}{\partial x} \bigg|_{x=0} \)

reactor pressure, Pa

partial pressure of species \( j \), Pa

capillary pressure, Pa

radial coordinate, m

ideal-gas constant or reactor radius, m

reaction rate, kmol/m³s

spreading factor, m

time, s

temperature, K

period of heaving/oscillating motion

interstitial velocity of \( \alpha \)-fluid, m/s

axial coordinate, m

Greek Letters

angle of packed-bed column inclination with respect to the horizontal plane

heat transfer coefficient at the gas-liquid interface, J/m²sK

amplitude of the angular motion

packed bed porosity, -

\( \alpha \)-phase holdup, -

SO₂ absorption reaction enthalpy, kJ/Kmol

\( \text{N}_2\text{O}_4 \) absorption reaction enthalpy, kJ/Kmol

radial effective thermal conductivity of \( \alpha \)-phase, J/msK

\( \alpha \)-phase dynamic viscosity, kg/ms

\( \alpha \)-phase effective viscosity (a combination of bulk and shear terms), kg/m s

\( \alpha \)-phase density, kg/m³

surface tension, N/m

azimuthal coordinate, m

Subscripts/Superscripts

gas phase

i gas-liquid interface

in scrubber inlet

ℓ liquid phase

r radial direction

trans transfer

z axial direction

w scrubber wall
References


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