

Article

Experimental Investigation of SO₂ Removal from Flue Gases by Cleaning with Solution of Lime Suspension and Formic Acid

Milan Milotić¹, Slavko Đurić¹, Zoran Čepić^{2,*}, Dragan Adamović², Boris Obrovski², Dragiša Đorđić³ and Milena Stošić²

- ¹ Faculty of Transport and Traffic Engineering, University of East Sarajevo, Vojvode Mišića 52, 74000 Dobož, Bosnia and Herzegovina; milan.milotic@sf.ues.rs.ba (M.M.); slavko.djuric@sf.ues.rs.ba (S.Đ.)
² Faculty of Technical Sciences, University of Novi Sad, Trg Dositeja Obradovića 6, 21000 Novi Sad, Serbia; draganadamovic@uns.ac.rs (D.A.); borisobrovski@uns.ac.rs (B.O.); milenastosic@uns.ac.rs (M.S.)
³ Faculty of Ecology, Independent University of Banja Luka, Veljka Mladenovića 12e, 78000 Banja Luka, Bosnia and Herzegovina; dragisa.djordic@nubl.org
* Correspondence: zorancepic@uns.ac.rs; Tel.: +381-642004875

Abstract: The experimental investigation presented in this research was performed in order to examine the possibility of the removal of SO₂ from flue gases by cleaning with a solution of lime suspension and formic acid (Ca(OH)₂ and HCOOH). Research was conducted in a laboratory plant (rotary kiln) of 44 kW. The mass of the lime suspension (LS) was 400 g. The mass of the LS was homogenized (mixed) in a sample cup with 2 g (0.5%), 4 g (1%) and 8 g (2%) of 60% formic acid. The solution was placed in a gas washing bottle, where a partial flow of flue gas generated by the combustion of diesel fuel was injected. Simultaneously with the diesel fuel combustion, SO₂ from a bottle was injected in a rotary kiln. The average mass concentration of SO₂ in the flue gas at the entry point of the gas washing bottle was around 2900 ppm. The results indicated that the absorption of SO₂ by the cleaning of flue gas with LS was 96.83%. Adding formic acid to the LS in mass ratios of 0.5% (2 g), 1% (4 g) and 2% (8 g) resulted in absorptions of 99.25%, 98.77% and 98%, respectively. The absorption of flue gases in the gas washing bottle with LS, with the addition of formic acid in the mentioned ratios, showed a reduction in sulfates and pH value, and a rise in sulfides and calcium, respectively.

Keywords: sulfur dioxide; flue gas desulfurization; lime suspension; formic acid; diesel fuel



Citation: Milotić, M.; Đurić, S.; Čepić, Z.; Adamović, D.; Obrovski, B.; Đorđić, D.; Stošić, M. Experimental Investigation of SO₂ Removal from Flue Gases by Cleaning with Solution of Lime Suspension and Formic Acid. *Processes* **2022**, *10*, 537. <https://doi.org/10.3390/pr10030537>

Academic Editors: Qingyue Wang, Weiqian Wang and Jayanto Kumar Sarkar

Received: 18 January 2022

Accepted: 3 March 2022

Published: 9 March 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The world's need for energy, electric energy in particular, is in a constant rise. Fossil fuel resources (coal, oil and gas) are being depleted. Fossil fuels are currently the main source of energy in the world. It is estimated that the world reserve of coal is 10¹² tons, that of natural gas is 340.6 × 10¹² m³, and that of oil is around 1.64 × 10¹²–1.66 × 10¹² barrels, including the reserves in oil shale [1,2]. The burning of fossil fuel, especially in thermal power plants (TPP), results in products such as SO_x (SO₂, SO₃), NO_x (NO, NO₂, N₂O), unburned hydrocarbons, fly ash and soot. Some of them are toxic, such as SO_x, NO_x, C_mH_n, CO, and fly ash. Sulfur dioxide is the most significant oxide of sulfur created by burning and is emitted into the atmosphere. Sulfur dioxide (SO₂), sulfur trioxide (SO₃), nitrogen monoxide (NO), nitrogen dioxide (NO₂) carbon monoxide (CO), carbon dioxide (CO₂), etc., produced by coal burning, accumulate in the atmosphere and create a greenhouse effect. Mixed with the moisture in the air, they create acid rains that destroy plants and erode rocks and buildings.

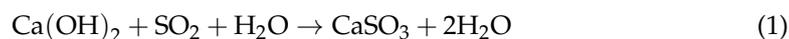
Due to the ever rising emission of gases in the atmosphere, especially SO₂, and stricter domestic and international regulations about air pollution [3,4] efforts are being made all over the world to reduce the emission of SO₂, be it from existing or new power and heating

plants. All existing methods used for the reduction in gas emission can be divided into three groups:

- (1) Methods applied before the burning process (washing or additive coal);
- (2) Methods applied during the burning process (fluidized bed combustion);
- (3) Methods applied after the burning process (flue gas desulfurization—FGD).

Depending on the type of the product, FGD procedures can be wet (the product is a sulfate suspension or slurry), semi dry and dry (the product is a dry matter). Compounds used as sorbents in wet procedures are mostly based on calcium (CaCO_3 , CaO , Ca(OH)_2 , and $\text{CaMg(CO}_3)_2$), magnesium, phosphoric and phosphate slurry because of their economic justification and the fact that the product, after a slight treatment, can be used as a building material.

For FGD processes with limestone, calcium hydroxide (Ca(OH)_2) is most commonly used:



In reference to the above, many researchers explore the use of compounds of calcium, magnesium and different organic acids as additives for the reduction in SO_2 from flue gases in thermal power plants.

Fernandes Pimenta [5] in her master's thesis explored the desulfurization of flue gases by adding organic acids: adipic acid, maleic acid and glutaric acid, each with concentration of 4.3 mmol/L, as well as CaO and Maalox (used as syrup in the treatment of gastric acid). The obtained results were compared in terms of lime conversion. Achieved level of desulfurization was higher than 99%, and the confirmed lime conversion was 100% and 93%, respectively, after adding 4.3 mmol/L of adipic acid or adding Maalox with 4.3 mmol Mg(OH)_2 per liter of suspension.

Vejvoda and Hubená in their monograph [6] stated the efficiency of FGD for three different desulfurization methods: dry fluidized bed combustion technology (efficiency 80–90%), semi dry limestone method (efficiency 60–90%) and wet limestone method (efficiency $\geq 96\%$).

Li et al. [7] researched the possibility of the removal of SO_2 from flue gases by the use of red mud. The combined application of red mud as sorbent with parallel removal of SO_2 and NO_x from flue gases is an innovative approach. During the investigation, flue gases were dampened with steam in order to increase the separation of SO_2 . Investigation included the measurement of red mud concentration, flue gas mass flow, liquid–gas ratio and SO_2 mass concentration. Results showed that the SO_2 removal efficiency depends primarily on the concentration of red mud sorbent, gas flow and liquid–gas ratio and that they were not pursuant to the industrial requirements. Improved removal of SO_2 from flue gas (even higher than 99%) is possible with the red mud concentration of 15%, gas flow of 40 L/min, liquid–gas ratio of 20 L/m³, sorbent renewal speed of 15% and sodium chlorite concentration of 1.9%. These research studies of the mentioned authors provide potentially feasible technology for the low-cost use of red mud for the simultaneous removal of SO_2 and NO_x from flue gases, instead of the use of conventional methods.

Liu et al. [8] concluded that when the flue gas contained CO_2 and SO_2 , they reacted with Ca(OH)_2 simultaneously to form calcium carbonate and sulfite, but part of the carbonate formed reacted further with SO_2 to form sulfite. The ratio of carbonate was significantly reduced with the reduction in SO_2 concentration in the range below 500 ppm, but the ratio of sulfide reduced very little, in the range below 100 ppm. In concentrations of $\text{SO}_2 \leq 100$ ppm, conversions of Ca(OH)_2 into carbonate could be achieved in the ratio comparable to or higher than most typical Ca(OH)_2 conversions for the removal of SO_2 with dry or semi-dry flue gas desulfurization processes. Research results of the mentioned authors could also be used to evaluate the possibility of the use of solid waste that contains CaO or Ca(OH)_2 for the reduction in CO_2 from flue gases.

Nie et al. [9] researched the simultaneous removal of SO_2 and NO_x from flue gases created by burning coal in medium and small boilers. Phosphoric and phosphate slurry

were used as additives. The results showed that it is possible to remove up to 100% of SO₂ and NO_x from the flue gases. Compared to the traditional purification method, this process can achieve simultaneous desulfurization and denitrification without the release of secondary pollutants to the environment and can be regarded as a new and economic technology for the efficient removal of SO₂ and NO_x in the industrial processes.

Čalaga [10] researched in her thesis the removal of SO₂ from flue gases created by ship engines by cleaning flue gases with sea water. The cleaning was made in a scrubber. Besides the alkaline property of the sea water, an important parameter is the salinity since they affect the ionic strength of the solution and contribute to a higher efficiency of SO₂ removal. In order to investigate the possibility of the use of sea water for scrubbing, the author made a desulfurization model in ChemCAD software. The simulation was run for sea water of different alkalinity and salinity values. The calculation was made for the flow of flue gas of 1000 m³/h. The results indicate that the sulfur ratio in the purified flue gas was reduced. The application of a scrubber with sea water is a highly practical solution on ship engines because it does not require the storage of a calcium-based sorbent and does not have gypsum as a byproduct. It is estimated that the use of a scrubber can reduce the concentration of SO₂ by 98%.

Jeong and Lee [11] researched the efficiency of the simultaneous removal of SO₂ and NO₂ by adding formic acid, acetic acid or propionic acid to the limestone (CaCO₃) slurry, but there are hardly any literature data on the improvement of SO₂ removal from flue gases by lime suspension with the addition of formic acid.

In this regard, a number of researchers [12–22] explored and developed a series of procedures for SO₂ reduction, in order to find the optimal and economic procedure. Having this in mind, the authors of this paper explored the possibility of the application of a solution of lime suspension and formic acid for the removal of SO₂ from flue gas since formic acid enhances the absorption process. The high-level efficiency of SO₂ removal from flue gas by the use of the mentioned solution and practical application in the SO₂ reduction from thermal energy plants, heating plants and, especially, thermal power plants was the main reason that inspired the authors to conduct this research.

2. Materials and Methods

2.1. Diesel Fuel

Diesel fuel, with the chemical properties given in Table 1, was used for the experimental investigation of the removal of SO₂ from flue gases by the solution of LS and formic acid. By comparing the chemical properties of diesel fuel with some alternative fuels, such as waste motor oil (WMO) and waste transformer oil (WTO), it is noticeable that properties of these oils are conformed. An increasing number of research studies in recent periods [23–27] have indicated that WTO and WMO, mixed with diesel fuel, can be used as an alternative fuel for low power heat generators, diesel engines, agricultural machines, individual and different kinds of industrial burners.

Table 1. Chemical properties of diesel fuel [28].

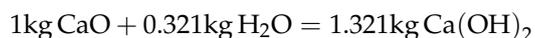
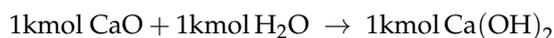
Element % _{wt}	Diesel Fuel	WMO	WTO	Method
C	85.76	85.47	86.31	ASTM D 5291 (Procedure A): 2016
H	14.00	12.64	12.51	ASTM D 5291 (Procedure A): 2016
N	0.20	0.12	0.02	ASTM D 5291 (Procedure A): 2016
S	0.0043	0.15	0.06	Own method
W	0.0080	0.52	0.55	-
A	0.0077	1.10	0.55	HRN EN 14,346 B 2007
O ¹	0.0200	0.00	0.00	HRN EN ISO 6245:2003
Lower heating value, kJ·kg ⁻¹	46066	44322	44124	ASTM D 240:2009

¹ By difference.

2.2. Lime Suspension

The lime suspension was prepared in the following way:

- (1) A mass of CaO (m_1) needed for the experiment was measured, $m_1 = 1$ kg. For this experiment, quicklime with the properties defined by standard BAS EN 459-1:2016 was used.
- (2) A mass of water (m_2) needed for lime slaking was measured. Mass, m_2 , was determined by the following formula:



which means that slaking of 1 kg of CaO requires 0.321 kg of water.

- (3) A mass of water ($m_3 = 15.179$ kg) needed for the production of LS with 8% slaked lime Ca(OH)_2 was measured.
- (4) Measured lime with mass m_1 was placed in a glass pot, and then a mass of water was added ($m_2 + m_3$), with intensive stirring of the LS in order to ensure proper lime slaking.

Figure 1 shows a photograph of the glass bottle with LS.

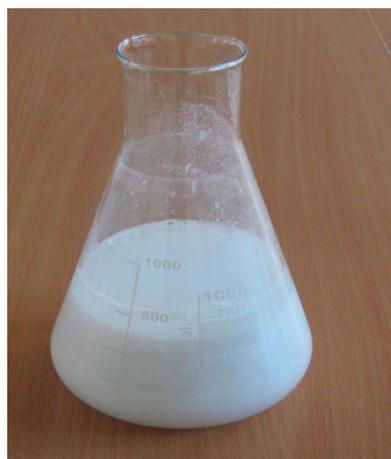
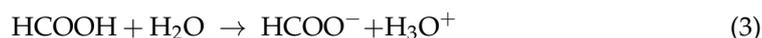


Figure 1. Prepared lime suspension.

2.3. Formic Acid (HCOOH)

Formic acid is a carboxylic acid and has a formula, HCOOH . It is a weak organic acid that coexists with its conjugated base in a water solution by the following formula:



It is produced as a byproduct of acetic acid. Formic acid is used in the production of raw rubber, tanning, wool dyeing, fruit juice conservation, etc. There are some attempts to use a mixture of lime suspension and formic acid for the removal of SO_2 from flue gas, given that formic acid enhances the absorption process of SO_2 . In small quantities, formic acid has an effect as a pH buffer [29]. For the purpose of the experimental investigation of flue gas cleaning in a gas washing bottle, 60% formic acid was used.

2.4. Experimental Plant

The experimental investigation of the removal of SO_2 from flue gases by cleaning with LS and a mixture of LS and formic acid was performed in a laboratory for combustion

and environmental protection at the Faculty of Transport and Traffic Engineering in Doboj, Bosnia and Herzegovina. The plant was set up and prepared to enable the reliable measurement of diesel fuel combustion process parameters, such as fuel consumption, continuous introduction of SO₂ into a rotary kiln, temperature in the rotary kiln, flue gas flow, excess air coefficient, and measurement of concentration of flue gas composition, as well as the parameters of cleaning of flue gases in a gas washing bottle. Setup of the experiment plant was the same for each measurement. Figure 2 shows the setup of the experiment plant with measurement points (M.P.). The plant consists of a 44 kW rotary kiln (4) with a burner (3) for the combustion of diesel fuel. Average mass fuel consumption during burning is measured with a scale (1). Besides the burner, SO₂ from a bottle (9) was injected into the kiln with a mass flow of 0.2 m³/h (10). Using a vacuum pump (15), a partial flow of flue gas (6) was separated, and, through smoke analysis bottle (7), the composition of the flue gases was determined. (8) The flue gases were cleaned in a gas washing bottle (11). At the exit of the gas washing bottle, after SO₂ absorption, the composition of flue gas was measured again (13).

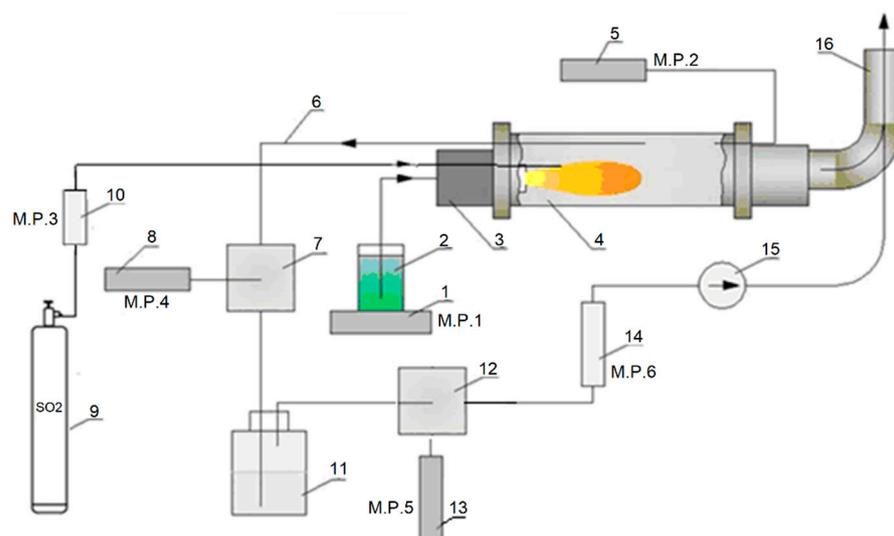


Figure 2. Scheme of a laboratory plant: 1—fuel consumption measuring device (M.P.1), 2—diesel fuel graduate, 3—burner, 4—rotary kiln, 5—temperature indicator (M.P.2), 6—partial flue gas flow, 7—smoke analysis bottle, 8—smoke analyzer (M.P.4), 9—SO₂ bottle, 10—rotameter, 11—flue gas washing bottle (SO₂ absorption), 12—smoke analysis bottle, 13—smoke analyzer (M.P.5), 14—rotameter (M.P.6), 15—vacuum pump, 16—exhaust pipe, M.P.1—fuel consumption; M.P.2—flue gas temperature in the rotary kiln, M.P.3—SO₂ mass flow, M.P.4—flue gas analysis (O₂, CO, CO₂, NO_x, SO₂, t) at the entry of the gas washing bottle, M.P.5—flue gas analysis (O₂, CO, CO₂, NO_x, SO₂, t) at the exit of the gas washing bottle; M.P.6—flue gas volumetric flow rate.

The following measurement instruments were used during the experimental investigation: digital scale UNIT, measurement range 0–5000 g, measurement error ± 1 g, for the measurement of fuel consumption (M.P.1); burner WL2V, Nr. O5164/68, power 44 kW; digital temperature gauge Testo 925 with a probe type K (NiCr-Ni), measurement range 50–1000 °C, measurement error $\pm 0.2\%$, (M.P.2); and smoke analyzer MULTILYZER STx for the measurement of composition of the sampled flue gas (M.P.4 and M.P.5), flue gas flow gauge (rotameter) TG 06, Nr. 45000, measurement range 200–2200 L/h, (M.P.3 and M.P.6).

Experimental investigation of SO₂ removal from flue gas was made with four different absorbents. The first one was LS with initial mass of 400 g, while the remaining three absorbents were a mixture of 400 g of LS and formic acid in a mass ratio of 0.5% (2 g), 1% (4 g) and 2% (8 g) of the initial mass of LS.

In order to obtain reliable measuring results, the experiment was repeated four times for each type of measurement. Results were consistent, and there was no significant

difference between them. Standard deviation (S) and coefficient of variation (Cv) were determined as a measure of the variability of obtained results.

3. Results and Discussion

3.1. Combustion Analysis

Average values of the most significant parameters of combustion for all stages of the experimental investigation are shown in Table 2.

Table 2. Fuel combustion parameters in 44 kW rotary kiln.

Parameter	LS	LS + 0.5% _{wt} HCOOH	LS + 1% _{wt} HCOOH	LS + 2% _{wt} HCOOH
Fuel mass flow, kg/h	3.06	2.76	2.94	3.12
Temperature in the rotary kiln, °C	532	546	554	570
S, °C	5.69	17.25	9.52	15.45
Cv, %	0.01	0.03	0.02	0.03
Temperature of the sampled gas, °C	26.72	31.92	31.15	28.62
S, °C	6.49	7.21	6.80	5.94
Cv, %	0.24	0.22	0.22	0.21
O ₂ in flue gas, %	10.10	10.62	10.12	9.85
S, %	0.00	0.1	0.05	0.06
Cv, %	0.00	0.01	0.01	0.01
Excess air coefficient, -	1.92	2.02	1.93	1.88
S, -	0.01	0.01	0.01	0.01
Cv, %	0.01	0.01	0.01	0.004
Flow rate, m ³ /h	0.52	0.51	0.51	0.50
S, m ³ /h	0.01	0.01	0.01	0.01
Cv, %	0.02	0.02	0.02	0.01

Fuel consumption was in a range from 2.76 kg/h to 3.12 kg/h. Average value of the excess air coefficient during diesel fuel combustion was in the range from 1.88 to 2.02. The flue gases' temperature in the rotary kiln was in the range from 532 °C to 570 °C, and the temperature at the exit of the gas washing bottle was in the range from 26.72 °C to 31.92 °C.

3.2. Emission Parameters

Table 3 shows the volume ratio of gas components (O₂, CO, CO₂, NO_x, and SO₂) before and after the cleaning of flue gases in the gas washing bottle.

Table 3. Emission parameters values before and after flue gases cleaning.

Before Cleaning of Flue Gases in the Gas Washing Bottle (M.P.4)				
O ₂ , %	8.10	8.10	8.10	8.10
CO, ppm	0.00	0.00	0.00	0.00
CO ₂ , %	11.30	11.30	11.40	11.30
NO _x , ppm	41.00	43.00	46.00	48.00
SO ₂ , ppm	2871	2882	2908	2940
After cleaning of flue gases in the gas washing bottle (M.P.5)				
	LS	LS + 0.5% _{wt} HCOOH	LS + 1% _{wt} HCOOH	LS + 2% _{wt} HCOOH
O ₂ , %	10.10	10.62	10.12	9.85
S, %	0.00	0.1	0.05	0.06
Cv, %	0.00	0.01	0.01	0.01
CO, ppm	0.00	0.00	0.00	0.00
S, ppm	0.00	0.00	0.00	0.00
Cv, %	0.00	0.00	0.00	0.00

Table 3. Cont.

After cleaning of flue gases in the gas washing bottle (M.P.5)				
	LS	LS + 0.5% _{wt} HCOOH	LS + 1% _{wt} HCOOH	LS + 2% _{wt} HCOOH
CO ₂ , %	9.60	9.12	9.55	9.80
S, %	0.08	0.05	0.06	0.00
C _v , %	0.01	0.01	0.01	0.00
NO _x , ppm	39.50	36.00	37.00	39.50
S, ppm	0.58	0.00	0.00	0.58
C _v , %	0.01	0.00	0.00	0.01
SO ₂ , ppm	91.00	22.00	36.00	59.00
S, ppm	1.41	5.66	5.48	1.73
C _v , %	0.02	0.08	0.07	0.02

3.2.1. Nitric Oxide (NO_x) Emission

NO_x emission before and after flue gases cleaning in the gas washing bottle are shown on Figure 3. It can be observed that the emission of NO_x before the cleaning of flue gases in the gas washing bottle is 14.3% higher than the emission after the cleaning. This result was expected, given the potential of NO_x to react with LS and formic acid.

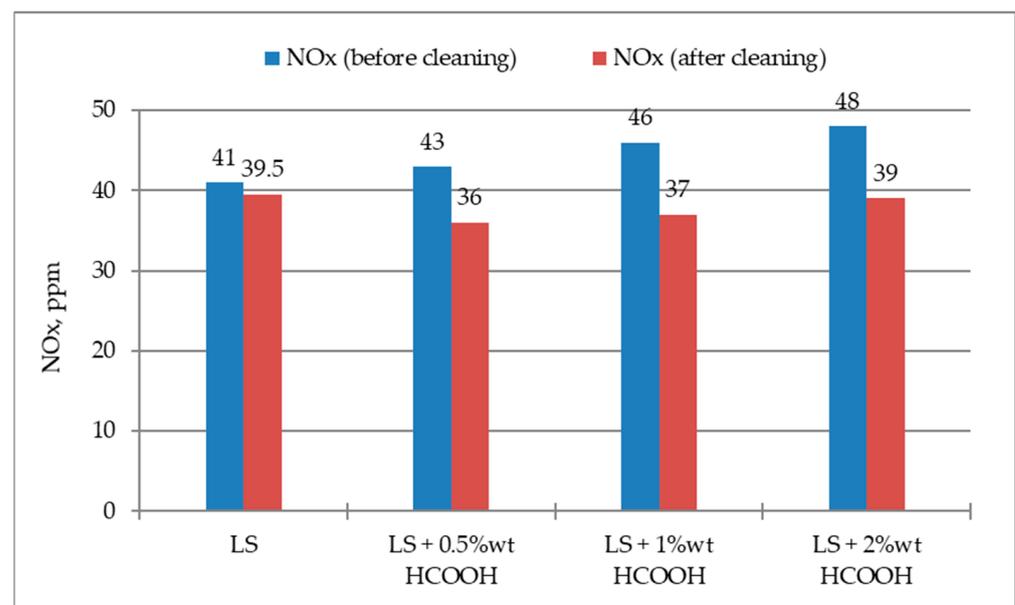


Figure 3. NO_x values before and after flue gases cleaning.

3.2.2. Carbon Monoxide (CO) and Carbon Dioxide (CO₂) Emission

Carbon monoxide (CO) is one of the most important pollutants produced by fuel combustion, as an indicator of incomplete combustion. During combustion, no emission of CO in flue gas was registered. This indicates that the burning in the rotary kiln was complete and that the rotary kiln burner was properly set.

CO₂ emission before and after flue gases cleaning in the gas washing bottle is shown on Figure 4. It can be observed that the emission of CO₂ before the cleaning of flue gases in the gas washing bottle is 16.1% higher than the emission after the cleaning. This result could be expected given the average temperature of the flue gas at the exit from gas washing bottle of around 30 °C and easy solubility of CO₂ in water of 1.45 g/L under standard conditions (25 °C and 101 kPa). CO₂ reacts with the LS, forming CaCO₃, as per the following reaction:



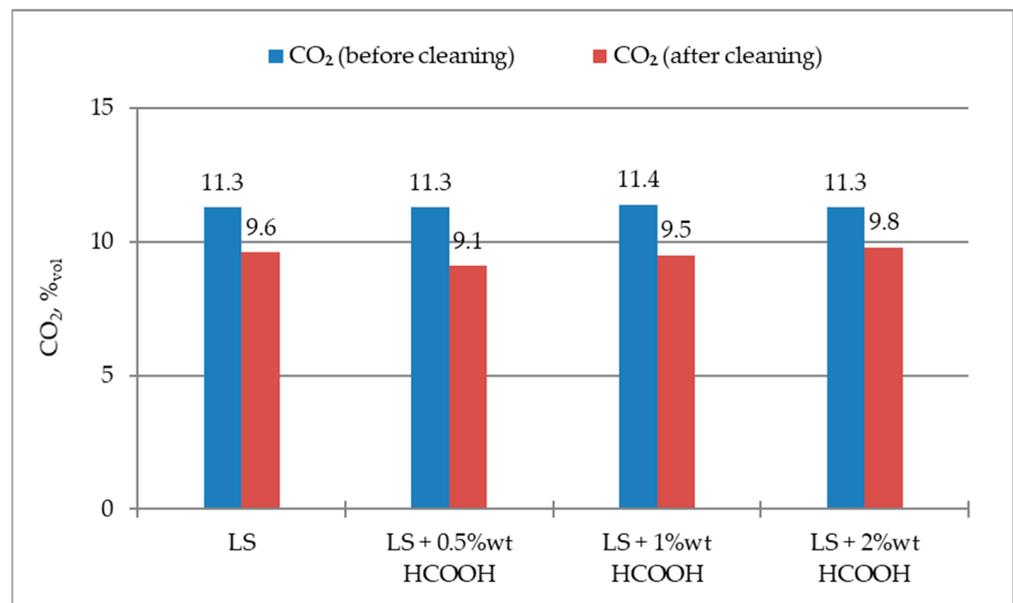


Figure 4. CO₂ values before and after flue gases cleaning.

3.2.3. Sulfur Dioxide (SO₂) Emission

The average value of SO₂ concentration in the flue gas at the entry of gas washing bottle (before cleaning of flue gas) was around 2900 ppm, and it is important for the SO₂ absorption process. An increase in the SO₂ concentration at the entry of gas washing bottle usually produces increased speed of SO₂ absorption, with a linear correlation observed in some cases.

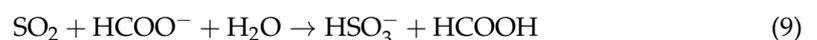
The following reactions take place in the absorption of SO₂ into aqueous Ca(OH)₂ solution:



Since the final reaction product, CaSO₃, is almost insoluble and the equilibrium constants for the first and second reactions are very large, the reactions can be replaced by the following reaction:



If a small amount of formic acid is added to the LS, an additional reaction is occurred:



where is HCOO[−] is a conjugate base of formic acid, as shown in Formula (3). As shown in reaction (9), SO₂ reacts with the HCOO[−] ion, generating a bisulfite ion and regenerating HCOOH. Therefore, the SO₂ absorption increases as reaction (9) is expedited [11].

Figure 5 shows the SO₂ concentration variation before and after flue gases cleaning for the LS and mixtures of LS with formic acid, as well the SO₂ absorption efficiency.

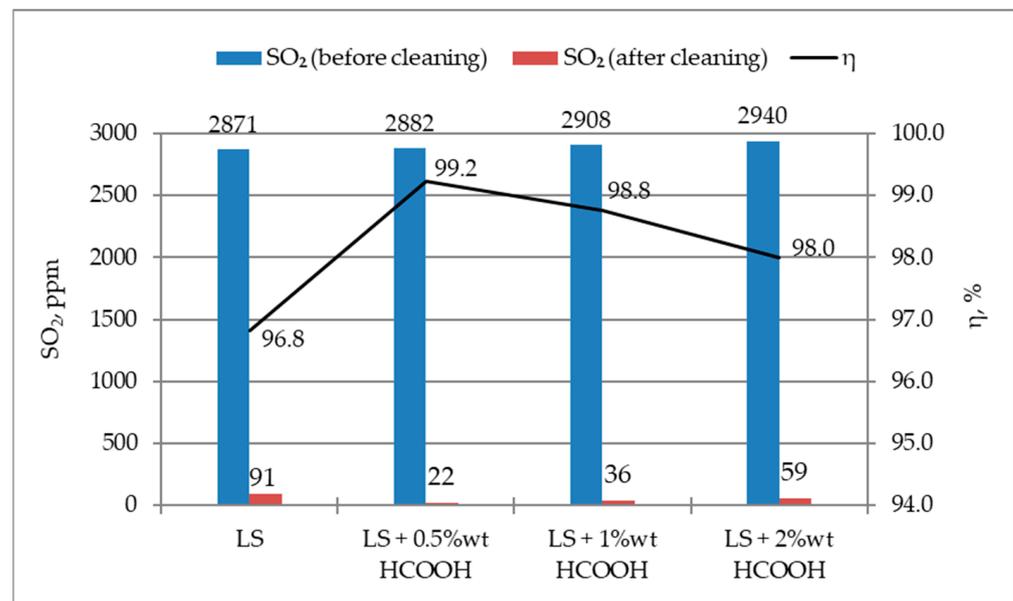


Figure 5. SO₂ values before and after flue gases cleaning and absorption efficiency.

The SO₂ absorption efficiency was determined by the following formula:

$$\eta_{\text{SO}_2} = \frac{C_{\text{SO}_2,\text{in}} - C_{\text{SO}_2,\text{out}}}{C_{\text{SO}_2,\text{in}}} \cdot 100, \% \quad (10)$$

where

$C_{\text{SO}_2,\text{in}}$ —SO₂ concentration at the entry of the gas washing bottle (before flue gases cleaning), in ppm;

$C_{\text{SO}_2,\text{out}}$ —SO₂ concentration at the exit of gas washing bottle (after flue gases cleaning), in ppm.

It can be observed in Figure 5 that the smallest value of SO₂ absorption efficiency of 96.83% was achieved with the use of LS. By adding 0.5% formic acid to the LS, the absorption efficiency increased to 99.25%, which is an increase in absorption efficiency of some 2.5%. With the further addition of formic acid to the lime suspension, the efficiency of SO₂ absorption from flue gases begins to decrease and has values of 98.8% and 98.0% for LS with 1% and 2% of HCOOH, respectively.

The increased absorption of SO₂ achieved by adding a small amount (0.5%) of formic acid in the gas washing bottle was expected because additives, such as formic acid, decrease the pH drop caused by the absorption of SO₂ in the suspension, leading to an increased mass transfer of SO₂ from the gas phase to the absorbent during the whole contact time between the suspension and flue gas, and subsequently improves the SO₂ removal efficiency [29]. The increase in the mass fraction of formic acid to 1% and 2% in the LS + HCOOH mixture led to the weaker formic acid effect as a pH buffer, and the pH value of the mixture began to decline, resulting in increased resistance to mass transfer and reduced absorption efficiency of SO₂ [30]. On the other hand, preliminary measurements showed that when the mass fraction of formic acid was less than 0.5% (tested with 0.2%), the pH value of the mixture (LS + HCOOH) was close to the pH value of the pure lime suspension, and the absorption efficiency of SO₂ was close to the desulfurization efficiency with pure LS.

Table 4 shows a comparison between the results of the SO₂ removal from flue gases presented in this paper and some data from the literature. It can be noted that the highest degree of SO₂ absorption from flue gas of 99.6% was achieved with the application of adipic acid, and the lowest value of 95% by the application of sea water. Glutaric acid and maleic acid also produced high levels of SO₂ absorption efficiency. If the average value of SO₂ absorption from the experiment is compared to the average value of SO₂ absorption from

the literature, an insignificant difference (around 1.3%) can be noted. This indicates that the results of SO₂ absorption with the mixture of LS and HCOOH are consistent with similar research studies presented in the scrutinized literature.

Table 4. Comparative data of SO₂ removal from flue gases by cleaning.

Absorption Efficiency	This Paper				Literature Data				
	LS	LS + 0.5%wt HCOOH	LS + 1%wt HCOOH	LS + 2%wt HCOOH	Seawater and Limestone [12]	Lime or CaO and Water [12]	Adipic Acid [5]	Glutaric Acid [5]	Maleic Acid [12]
η_{SO_2} , %	96.83	99.25	98.77	98.00	90–95	90–95	99.2–99.6	98.9–99.6	98.1–98.9

3.3. Cleaning of Flue Gases

The absorption of flue gases was done in a gas washing bottle (11) (see Figure 2) with LS and a mixture of LS with specific mass ratios of formic acid. The purpose of cleaning was to remove SO₂ from the flue gas and determine the composition of the mixture after the cleaning process. The following parameters were determined: sulfates, pH value, sulfides and calcium [31]. The results are shown in Figures 6–9.

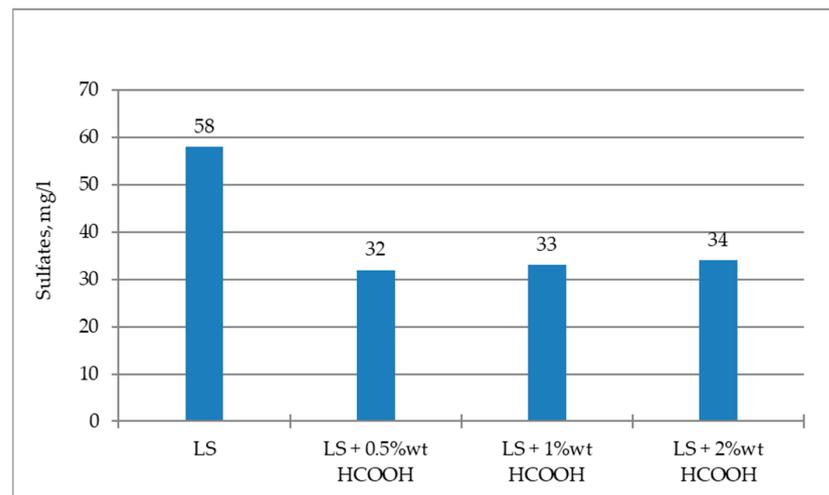


Figure 6. Sulfates in the washing bottle after flue gas cleaning.

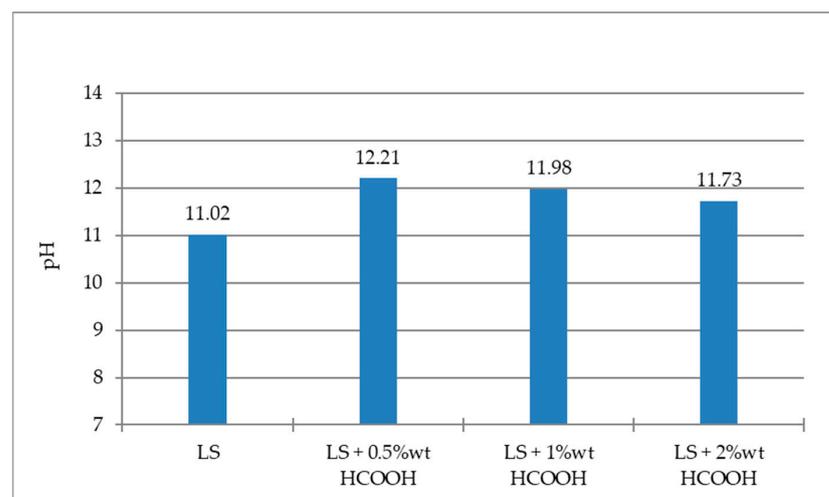


Figure 7. The pH in the washing bottle after flue gas cleaning.

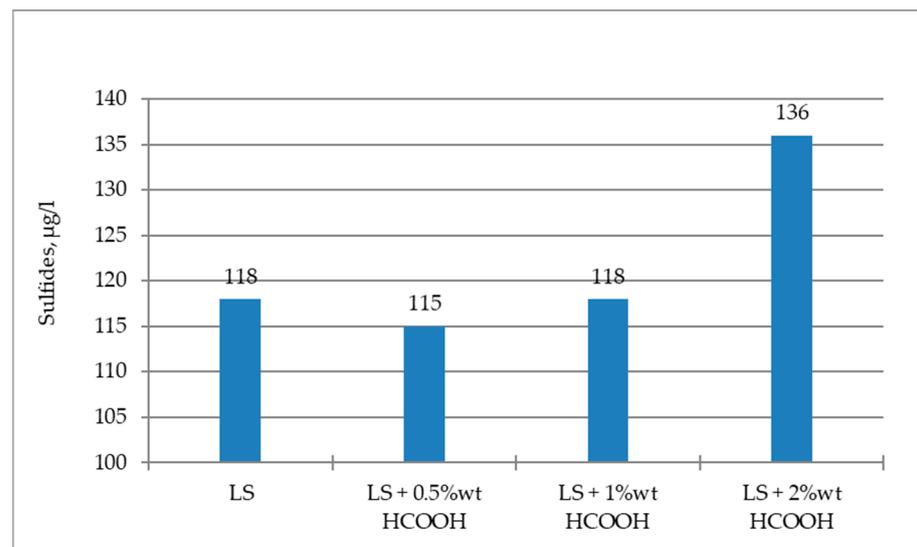


Figure 8. Sulfides in the washing bottle after flue gas cleaning.

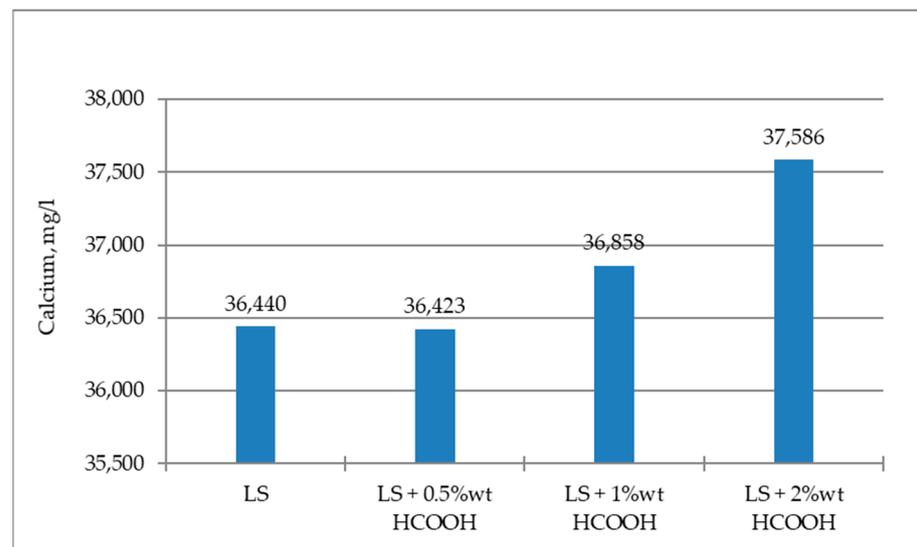


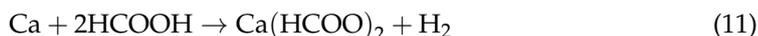
Figure 9. Calcium in the washing bottle after flue gas cleaning.

The presence of all scrutinized parameters was detected in the gas washing bottle. The highest sulfate concentration of 58 mg/L in the gas washing bottle was detected in the LS, and the lowest of 32 mg/L in the mixture of LS + 0.5%_{wt} HCOOH. In other solutions, LS + 1%_{wt} HCOOH and LS + 2%_{wt} HCOOH, a slight increase in sulfate was detected (Figure 6). Sulfate in water (solution) increased the acidity of the solution, which is indicated by the decrease in pH value of the observed solutions (Figure 7).

In all experiments, the results showed an alkaline environment with a pH value in the range from 11.02 for LS to 12.21 for the mixture LS + 0.5%_{wt} HCOOH (Figure 7). An alkaline environment is favorable for the removal of SO₂ during the cleaning of flue gas [30], which can be observed in Figure 5.

Figure 8 shows the increase in sulfide in the gas washing bottle during flue gases cleaning. The highest concentration of sulfide in the gas washing bottle of 136 µg/L was detected in the mixture LS + 2%_{wt} HCOOH, and the lowest value of 115 µg/L in the mixture LS + 0.5%_{wt} HCOOH. As expected, the highest concentration of sulfide in the gas washing bottle was in the mixture of LS + HCOOH, given the physical and chemical properties of sulfides.

Figure 9 shows the ratio of calcium in the gas washing bottle after flue gases cleaning. A slight increase in the calcium ratio was observed in the solution (in gas washing bottle) when the ratio of formic acid was increased in the LS. With the ratio of formic acid in the LS of 2% (8 g), the ratio of calcium was 3758 mg/L, which is around 3% more than the ratio of calcium in the LS with 0.5% (2 g) of formic acid. A slight increase in the calcium ratio in the gas washing bottle was expected, given the chemical bonding of calcium in the lime paste with formic acid. Balanced reactions are presented by the following formulae:



4. Conclusions

This paper presents the results of an experimental investigation of the desulfurization of flue gases from a 44 kW rotary kiln. The partial flow of flue gas created by the combustion of diesel fuel, with a simultaneous addition of SO₂ into the rotary kiln, was introduced into the gas washing bottle, where flue gases were cleaned. The cleaning of flue gases was performed with four absorbents, a lime suspension and mixtures of a lime suspension and formic acid, where formic acid was used in mass ratios of 0.5% (2 g), 1% (2 g) and 2% (8 g) of the LS mass (400 g). The following conclusions were made:

- The investigation showed that adding formic acid to the lime suspension (in the mentioned mass ratios) increases SO₂ absorption in the gas washing bottle. SO₂ absorption efficiency obtained using only LS was 96.83%, and the highest value of SO₂ absorption efficiency (99.25%) was achieved using a mixture of LS and 0.5% (2 g) of HCOOH, which increased the absorption efficiency by around 2.5%. Mixtures of LS with 1% (4 g) and 2% (8 g) HCOOH also caused the increase in SO₂ absorption efficiency, compared with LS, but less than the mixture of LS and 0.5% of HCOOH. An increase in the SO₂ absorption by adding formic acid (HCOOH) to the LS was expected, given the fact that formic acid in small quantities has an effect as a pH buffer.
- The concentrations of CO₂ and NO_x before the cleaning of flue gases were 16.1% and 14.3%, respectively, higher than the concentrations after the cleaning.
- The highest sulfate concentration of 58 mg/L in the gas washing bottle was detected in the LS, and the lowest of 32 mg/L in the mixture of LS + 0.5% HCOOH. In other solutions, LS + 1% HCOOH and LS + 2% HCOOH, a slight increase in sulfate was detected. Sulfate in water (solution) increases the acidity of the solution, which is indicated by the decrease in pH value of the observed solutions.
- On the basis of the experiments, it can be concluded that adding 2% (8 g) of HCOOH to the LS in the gas washing bottle significantly increases the ratio of sulfide, by some 15%, in comparison to the LS, where the amount of sulfide is 118 µg/L.
- An increase in the ratio of formic acid in LS (from 0.5% to 2%) causes an increase in calcium in the solution (in the gas washing bottle) by around 3%.

Therefore, for practical and economic reasons, it can be concluded that the amount of 0.5% (2 g) of HCOOH should be selected for further investigation, given the highest efficiency of SO₂ absorption of 99.25%, which is around 2.5% more than when a lime suspension is used without formic acid for which the SO₂ absorption from flue gases efficiency was 96.83%.

Author Contributions: Conceptualization, S.Đ., M.M. and Z.Č.; methodology, S.Đ., M.M. and Z.Č.; formal analysis, M.M. and D.Đ.; investigation, S.Đ., M.M., Z.Č. and D.Đ.; data curation, D.A., B.O. and M.S.; writing-original draft preparation, S.Đ., M.M. and Z.Č.; visualization, D.A., B.O. and M.S.; supervision, S.Đ. and Z.Č. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This research was partially supported by the Ministry of Education, Science and Technological Development of Republic of Serbia through project No. 451-03-68/2022-14/200156.

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

References

1. Morales Pedraza, J. *Conventional Energy in North America: Current and Future Sources for Electricity Generation*, 1st ed.; Elsevier: Amsterdam, The Netherlands, 2020; pp. 155–209, ISBN 978-0-12-814889-1.
2. Haider, W.H. Estimates of Total Oil & Gas Reserves in The World, Future of Oil and Gas Companies and SMART Investments by E. & P. Companies in Renewable Energy Sources for Future Energy Needs. In Proceedings of the International Petroleum Technology Conference, Dhahran, Saudi Arabia, 13–15 January 2020, IPTC-19729-MS.
3. Regulation on Emission's Limiting Values into the Air from the Combustion Plant. Official Gazette of Federation of Bosnia and Herzegovina, no. 3/13 and 92/17, 2017. Available online: <https://leap.unep.org/countries/ba/national-legislation/regulation-emission-limit-values-combustion-plants> (accessed on 2 March 2022).
4. Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) (Recast) (Text with EEA relevance). *Official Journal of the European Union*, 6 January 2011.
5. Fernandes Pimenta, M. Flue Gas Desulphurization through Wet Limestone Process—Adding Acids and Bases to the Limestone Suspension. Master's Thesis, Department of Chemical Engineering, The Faculty of Engineering of the University of Porto, Porto, Portugal, 2010. Available online: <https://repositorio-aberto.up.pt/bitstream/10216/60197/1/000144793.pdf> (accessed on 2 March 2022).
6. Vejvoda, J.; Hubená, J. *Technologie a Aparáty Mokřých Vápno-Vápencových Procesů Odsiřování Spalin*; Monografie č. 7; Ústav pro Výzkum a Využití Paliv: Prague, Czech Republic, 1988; 98p.
7. Li, C.; Sheng, Y.; Sun, X. Simultaneous Removal SO₂ and NO_x by a Combination of Red Mud and Coal Mine Drainage. *Environ. Eng. Sci.* **2019**, *36*, 444–452. [\[CrossRef\]](#)
8. Liu, C.-F.; Shih, S.-M.; Huang, T.-B. Effect of SO₂ on the Reaction of Calcium Hydroxide with CO₂ at Low Temperatures. *Ind. Eng. Chem. Res.* **2010**, *49*, 9052–9057. [\[CrossRef\]](#)
9. Nie, Y.; Wang, X.; Dai, J.; Wang, C.; He, D.; Mei, Y. Mutual promotion effect of SO₂ and NO_x during yellow phosphorus and phosphate rock slurry adsorption process. *AIChE J.* **2021**, *67*, e17236. [\[CrossRef\]](#)
10. Čalaga, B. Removal of SO₂ from Flue Gases of Ship Engines by Cleaning with Sea Water. Master's Thesis, Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb, Croatia, 2016. Available online: <https://urn.nsk.hr/urn:nbn:hr:149:294125> (accessed on 2 March 2022).
11. Jeong, J.E.; Lee, C.-Y. The simultaneous removal of sulfur dioxide and nitrogen dioxide by the limestone slurry with addition of organic acid additives. *Korean J. Chem. Eng.* **2021**, *38*, 2064–2071. [\[CrossRef\]](#)
12. Poullickas, A. Review of Design, Operating and Financial Considerations in Flue Gas Desulfurization Systems. *Energy Technol. Policy* **2015**, *2*, 93–103. [\[CrossRef\]](#)
13. Jiang, L.; Mei, K.; Chen, K.; Dao, R.; Li, H.; Wang, C. Design and Prediction for Highly Efficient SO₂ Capture from Flue Gas by Imidazolium Ionic Liquids. *Green Energy Environ.* **2020**, *7*, 130–136. [\[CrossRef\]](#)
14. Koehler, M.; Ohle, A.; Bernhardt, D.; Gebauer, K.; Beckmann, M.; Kaiser, M.; Spiegel, W. A Survey on Methods for Analysis and Conservation of Hydrated Lime Particles Sampled in Flue Gas Cleaning Systems. *Ind. Eng. Chem. Res.* **2018**, *57*, 14854–14860. [\[CrossRef\]](#)
15. Nie, Y.; Li, S.; Dai, J.; He, D.; Mei, Y. Catalytic effect of Mn²⁺, Fe³⁺ and Mg²⁺ ions on desulfurization using phosphate rock slurry as absorbent. *Chem. Eng. J.* **2020**, *390*, 124568. [\[CrossRef\]](#)
16. Guo, H.; Zhou, S.; Shreka, M.; Feng, Y. A Numerical Investigation on the Optimization of Uneven Flow in a Marine De-SO_x Scrubber. *Processes* **2020**, *8*, 862. [\[CrossRef\]](#)
17. Szlugaj, J.; Galos, K. Limestone Sorbents Market for Flue Gas desulfurization in Coal-Fired Power Plants in the Context of the Transformation of the Power Industry—A Case of Poland. *Energies* **2021**, *14*, 4275. [\[CrossRef\]](#)
18. Deng, Y.; Ansart, R.; Baeyens, J.; Zhang, H. Flue Gas Desulphurization in Circulating Fluidized Beds. *Energies* **2019**, *12*, 3908. [\[CrossRef\]](#)
19. Tao, L.; Wang, X.; Ning, P.; Wang, L.; Fan, W. Removing sulfur dioxide from smelting flue and increasing resource utilization of copper tailing through the liquid catalytic oxidation. *Fuel Process. Technol.* **2019**, *192*, 36–44. [\[CrossRef\]](#)
20. Iliuta, I.; Iliuta, M.C. Modeling of SO₂ seawater scrubbing in countercurrent packed-bed columns with high performance packings. *Sep. Purif. Technol.* **2019**, *226*, 162–180. [\[CrossRef\]](#)
21. Hao, R.; Wang, X.; Mao, X.; Tian, B.; Zhao, Y.; Yuan, B.; Tao, Z.; Shen, Y. An integrated dual-reactor system for simultaneous removal of SO₂ and NO, Factors assessment, reaction mechanism and application prospect. *Fuel* **2018**, *220*, 240–247. [\[CrossRef\]](#)
22. Park, H.W.; Uhm, S. Various technologies for simultaneous removal of NO and SO₂ from flue gas. *Appl. Chem. Eng.* **2017**, *28*, 607–618.

23. Đorđić, D.; Milotić, M.; Čurguz, Z.; Đurić, S.; Đurić, T. Experimental Testing of Combustion Parameters and Emissions of Waste Motor Oil and Its Diesel Mixture. *Energies* **2021**, *14*, 5950. [[CrossRef](#)]
24. Yildiz, A.; Altun, S. The use waste transformer oil as alternative fuel in diesel power generator. *Int. J. Automot. Eng. Technol.* **2019**, *8*, 117–124. [[CrossRef](#)]
25. Djordjic, D.; Djuric, S.; Curguz, Z.; Hadzistevic, M. Experimental revitalisation test of waste transformer oil in Republika Srpska (Bosnia and Herzegovina). *J. Environ. Prot. Ecol.* **2019**, *20*, 862–887.
26. Behera, P.; Murugan, S. Combustion, performance and emission parameters of used transformer oil and its diesel blends in a DI diesel engine. *Fuel* **2013**, *104*, 147–154. [[CrossRef](#)]
27. Saidulu, E.; Dattatreya, G.S.G. Performance evaluation and emission characteristics of a waste transformer oil as an alternative fuel for diesel engine. *Int. J. Emerg. Trends Technol. Comput. Sci.* **2015**, *4*, 33–41.
28. Laboratory for Testing Water, Hydrocarbons and Materials. *Testing and Measurement Report; INA-Oil Industry*: Zagreb, Croatia, 2017.
29. Heidel, B.; Hilber, M.; Scheffknecht, G. Impact of additives for enhanced sulfur dioxide removal on re-emissions of mercury in wet flue gas desulfurization. *Appl. Energy* **2014**, *114*, 485–491. [[CrossRef](#)]
30. Zhang, L.; Wu, S.; Gao, Y.; Sun, B.; Luo, Y.; Zou, H.; Chu, G.; Chen, J. Absorption of SO₂ with calcium-based solution in a rotating packed bed. *Sep. Purif. Technol.* **2019**, *214*, 148–155. [[CrossRef](#)]
31. *Laboratory Analysis Reports, No. 07-10/2021*; Laboratory for Monitoring of Environment, Department of Environmental Engineering and Occupational Safety and Health, Faculty of Technical Sciences, University of Novi Sad: Novi Sad, Serbia, 2021.