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Bench- and Pilot-scale Investigation of Integrated Removal of Sulphur Dioxide, Nitrogen Oxides and Mercury in a Wet Limestone Scrubber

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1. Introduction

The reduction of sulphur dioxide (SO_2), nitrogen oxides (NO_x) and mercury (Hg) emissions is an important concern to environmental pollution. During recent years, the relevance of these pollutants to societal environmental issues and human health concerns has become increasingly apparent. Additionally, regulations such as the European Union directive on Large Combustion Plants (LCP, 2001/80/EC), the directive on Industrial Emissions (IED) and the United States Clean Air Transport Rule (CATR) require further emission reduction of these pollutants [5, 7, 19]. SO_2, NO_x and Hg are primarily released during coal combustion processes in the energy sector. Coal is main fuel of the Polish power sector – more than 90% of Polish power stations are coal-fired [13]. In the absence of national policies and binding international agreements concerning the limitation or reduction of greenhouse gas emissions, world coal consumption is projected to increase approximately 56% from 2007 to 2035 [11]. Increasing demand for energy to fuel electricity generation and industrial production in the region is expected to be met in large part by coal. Coal-fired generation increases by an annual average of 2.3%, making coal the second fastest-growing source for electricity generation in the IEA projection [11]. The environmental and health issues motivate the development of „clean coal technologies" with capture and sequestration of CO_2, and also the development of flue gas cleaning technologies from coal-fired boilers. EU Directive LCP, became effective in 2016 and required to limit NO_x and SO_2 to 200 mg/Nm^3 concentrations from large coal-fired boilers. This demands require a further investment in secondary methods of NO_x cleaning, [7, 15] because commercially available primary methods of NOx reduction are not able to obtain these emission limits. United States Environmental Protection Agency has recently proposed the Clean Air Transport Rule (CATR) (to replace EPA's 2005 Clean Interstate Rule). CATR requires reduction of NO_x and SO_2 emissions – 71% for SO_2 and 52% for NO_x – from 2005 levels [5]. Because of these large emission reduction requirements, a significant increase in the use of wet-FGD technology is expected over the next decade. EPA has also indicated an intention to regulate emission of Hg and other hazardous air pollutants (HAPs) from coal-fired electric utility boilers [21].

Most Polish coal-fired utility boilers use the primary methods of NOx control, as low-NO_x burners or the modification of combustion processes, but they are not able to reduce NO_x emission to that required by the LCP directive level. Commercially available secondary methods of NO_x control are selective catalytic reduction (SCR) using ammonia and selective non-catalytic reduction (SNCR) using urea. Additional methods of secondary NO_x control are sorption methods and electro-beam technologies [4, 6, 20, 22]. Another option is multipollutant control, in which a minimum of two pollutants can be captured by one device. Different types of multipollutant control techniques have been intensively developed over the last several years [1, 4, 8÷10, 12, 14]. The concept of multipollutant control in a wet scrubber seems to be one of the most interesting and is the subject of intensive reseach [1, 8, 10, 12]. Wet scrubbers are the most popular flue gas desulphurization system worldwide, for example, in the US 86% of all installed flue gas desulphurization systems are wet-scrubbed, and almost 70% of those wet scrubbers use the limestone process [17].

This paper presents results on the simultaneous removal of SO_2 with NOx and Hg in a wet limestone scrubber. Experiments were performed at bench and pilot-scale on simulated coal-fired flue gas. Sodium chlorite, as the most effective among tested oxidant additives, was used in most experiments to enhance the effectivenss of the wet limestone scrubber. The research is focused on achieving maximum NO_x, Hg and SO_2 removal efficiencies from flue gas, which may aid in the fullfillment of regulatory requirements. Parameters that can affect the removal process and which might be present in real conditions are also examined.

2. Experimental set-up and procedures

2.1 Bench-scale experimental set-up and procedure

The schema of the bench-scale apparatus is presented in Fig. 1. The system consists of a flow-through, bubble-type impinger to simulate a wet flue gas desulphurization scrubber. Simulated flue gas is generated from a controlled mixture of gas cylinders. Simulated flue gas comprised of approximately 81 vol% N_2, 11 vol% CO_2, 8% O_2, 0÷2500 ppm SO_2, 200 ppm NO, 206 $\mu g/m^3$ Hg^0. Elemental mercury vapor (Hg^0) was supplied using a VICI Metronics Dynacalibrator permeation oven held at 100°C and using N_2 as the carrier gas. The Hg concentration (206 $\mu g/m^3$) was 10 times higher than is typical for a coal combustion flue gas to accommodate the sensitivity of the mercury analyzer. The total flue gas components were measured online by series of analyzers. The NO_x species were measured using a continuous chemiluminescence NO_x analyzer (API: Advanced Pollution Instrumentation, Inc. model 200AH). The SO_2 species were measured using a continuous SO_2 fluorescence analyzer (API model 100AH). Hg^0 vapor was measured using a continuous cold vapor atomic absorption (CVAA) analyzer (BUCK model 400A). This instrument uses atomic absorption to quantify Hg^0 by producing an output signal between 0 and 250 mV that is proportional to the concentration. Both water and SO_2 interfere with Hg measurement by absorbing light at the wavelength being measured. Water was eliminated from the sample with the in-line Permapure Nafion dryer. SO_2 was an integral part of the flue gas being tested and produces a CVAA signal proportional to the SO_2 concentration. The SO_2 concentration was determined using the same sample stream as analyzed for Hg concentration (i.e., the SO_2 analyzer was installed in series, downstream of the CVAA analyzer). The CVAA response to SO_2 was determined daily, and Hg concentrations are subsequently corrected for SO_2 interference. To prevent long-term instrument drift, the sample cell from the CVAA analyzer was removed, soaked in a 10% nitric acid solution for at least 4 h, rinsed, and dried between each experiment. All analyzer results were automatically logged to a data acquisition system every 10 s. Prior to entering analyzers, the sample gas

was passed through a mini-impinger containing quartz wool to remove any water mist. The scrubbed gas then passed through heat traced lines to a Nafion dryer which removed remaining any remaining water vapor. The scrubber slurry was keep at 55°C by immersing the scrubber, to the overflow level, in a controlled temperature water bath and controlled by a thermocouple, connected to the data acquisition system.

Experiments to evaluate the influence of slurry pH were conducted in another flow-through, bubble-type of impinger simulating scrubber, where a thermocouple and self-cleaning electrode was placed constantly in the scrubber. These were connected to the auto-pH control system analyzing and regulating pH of the slurry automatically. The auto-pH control system consists of a Jenco pH controller with a Jenco Flat Tip Self Cleaning Industrial electrode and thermocouple and a control pH solution by continuously addition proper amount of H_3PO_4 or KOH solution via peristalsis pumps (Cole Parmer, Co. USA). Phosphoric acid (H_3PO_4) and potassium hydroxide (KOH) were used for pH control. All results were automatically logged to a data acquisition system every 10 s.

Oxidants (primarily $NaClO_2$, but also $NaClO_3$, $Ca(OCl)_2$, H_2O_2, NaOCl, $KMnO_4$) were tested and a calcium carbonate solution ($CaCO_3$) was blended prior to introduction to the scrubber using peristaltic pumps. The addition rate of the oxidant solution was monitored via weight loss in the beaker. The addition rate of the alkali solution was monitored via the weight gain from the overflow of the scrubber. The alkali scrubber solution was constantly mixed to ensure a homogeneous 10 wt% solids slurry. The majority of the work in these tests involved $NaClO_2$ as oxidizing additive. Liquid samples from tests were analyzed as soon as was practical for chloride, sulfate, nitrate, and nitrite by ion chromatography (IC) using EPA reference method 300.0. The samples were also analyzed for total Hg content. The samples were prepared for Hg analysis by aliquoting 10 mL of the solids slurry into digestion tubes and digesting according to ASTM method D6784-02 (Ontario Hydro) as described for the potassium chloride fraction. Hg analysis of each digest was carried out by CVAA according to EPA SW846 method 7470A "Mercury in Liquid Waste (Manual Cold Vapor Technique)." A Perkin-Elmer FIMS 100 flow injection mercury system was used for this analysis.

The tests were performed by allowing the simulated scrubber to overflow while the simulated flue gas stream bypassed the system – see Fig. 1. When the concentrations of all simulated flue gas components and the slurry temperature were steady for a minimum of 20 minutes, simulated flue gas was pulled into the simulated scrubber. The simulated flue gas continuously flowed through the scrubber with a flow rate of 2L/min by 60 minutes. A stirrer was used to help agitate gas and liquid phases. The stirring speed of the liquid phase and gas phase was the same for all experiments. The fresh $NaClO_2/CaCO_3$ slurry solution was added at a constant rate during the scrubbing period. The scrubber effluent was collected in a glass sample bottles during a timed 10 min interval near the end of the 60 min scrubber operation. The sample was immediately weighed, and it was placed on ice to quench or slow any oxidation reactions. The samples were then analyzed as soon as was practical for chloride, chlorite, chlorate, sulfate, nitrate, and nitrite by ion chromatography (IC) using EPA reference method 300.0. The sample was also analyzed for total Hg content. The samples were prepared for Hg analysis by aliquoting 10 mL of the solids slurry into digestion tubes and digesting according to ASTM method D6784-02 (Ontario Hydro) as described for the potassium chloride fraction. Analysis was carried out according to procedures mentioned in above section.

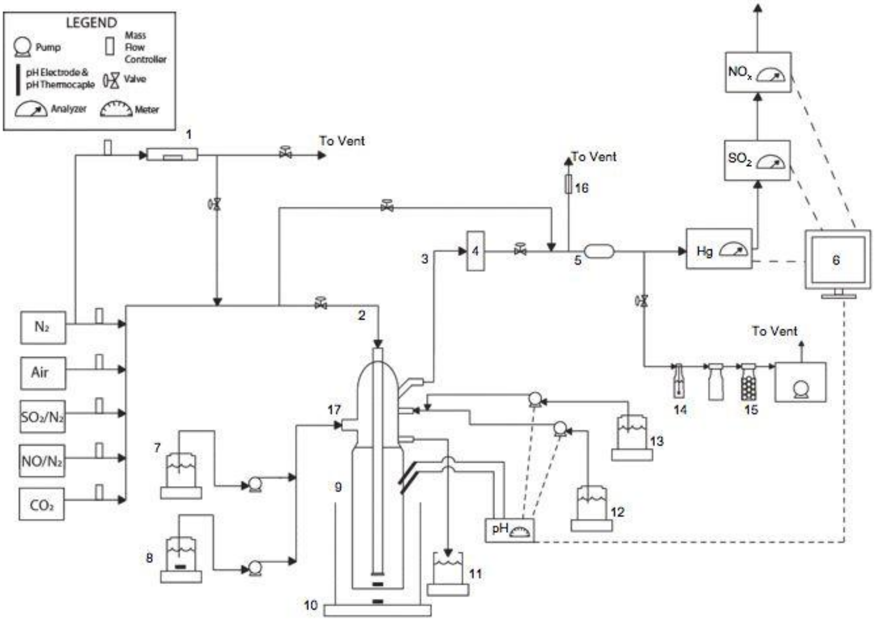

Fig. 1. Bench-scale experimental schema; 1 – Hg Permeation Oven, 2 – Gas Inlet, 3 – Gas Outlet, 4 – Filter, 5 – Naftion Dryer, 6 – Data Acquisition System, 7 – Oxidant w. Balance, 8 – Limestone Slurry w. Stir Plate, 9 – Scrubber, 10 – Heat and Stir Plate, 11 – Hold Tank w. Balance, 12 – Base Tank w. Balance, 13 – Acid Tank w. Balance, 14 – KiBC Bottle, 15 – Silica Bottle, 16 – Rotameter, 17 – Slurry Inlet

Rys. 1. Schemat stanowiska badawczego; 1 – komora permeacyjna Hg, 2 – wlot gazów, 3 – wylot gazów, 4 – filtr, 5 – osuszacz gazów Naftion, 6 – system gromadzenia danych, 7 – utleniacz na wadze laboratoryjnej, 8 – zawiesina wapniaka na płycie grzejnej z mieszadłem magnetycznym, 9 – skruber, 10 – płyta grzejna z mieszadłem, 11 – zbiornik z zawiesiną węglanu wapnia na mieszadle magnetycznym, 12 – zbiornik z roztworem zasady na wadze laboratoryjnej, 13 – zbiornik z roztworem kwasu na wadze laboratoryjnej, 14 – butla z KiBC, 15 – butla z krzemionką, 16 – rotametr, 17 – wlot zawiesiny

2.2 Pilot-scale experimental set-up and procedure

The pilot-scale scrubber system is presented in Fig. 2. The spray tower consists of three absorbers intended for scrubbing NO, Hg, and SO_2. Each absorber is 10 cm in diameter, 92 cm in length, and contains a 20 cm deep bed of plastic hollow balls (2 cm in diameter). The hallow balls are supported by a grid at the bottom of each absorber and are fluidized by the upward flue gas. The hollow balls, fluidized by the upward flue gas, facilitate slurry turbulence and promote intimate contact between the flue gas and scrubbing slurry so as to improve the pollutant removal efficiencies. The system was operated in the forced oxidation mode during experiments. Simulated flue gas was generated from a down-fired cylindrical furnace, known as an innovative furnace reactor (IFR). The fuel was introduced at the top of the furnace and combusted with air from axial and tangential directions. Since the natural gas-derived flue gas contained no SO_2 and only small amounts of NO, these components were added from gas cylinders to achieve the desired flue gas concentrations. When needed, a mercuric chloride ($HgCl_2$) solution (i.e., a dilute aqueous solution of $HgCl_2$) was used as the source of Hg^{2+} and was delivered by a peristaltic pump to the middle stage of the spray tower at a constant rate (5 mL/min). Gaseous Hg^0 was produced in a permeation oven (VICI Metronics Dynacalibrator) and was carried by air into the duct before the scrubber. Unless otherwise indicated, the simulated flue gas contains approximately 7 percent O_2, 7 percent CO_2, 550 to 2000 ppm SO_2, 220 ppm NO, and 17 $\mu g/m^3$ Hg. The total flow of flue gas is controlled at 800 ± 50 L/min. The concentrations of Hg, SO_2, and NO_x are continuously monitored at both the scrubber inlet and outlet using continuous emission monitoring systems (CEMS). Measurements of Hg^0 are performed using ultraviolet (UV) spectrometers (Seefelder-Hg 3000). Hg in the scrubber liquor is measured, when required, by cold vapor atomic absorption (CVAA) analyzer following EPA method 7040A. The NO_x species are monitored by an NO_x analyzer (API model 200AH) while SO_2 is measured by a fluorescence analyzer (API model 100AH). Under forced oxidation operation, slurry is not discharged to the slurry hold tank at the bottom., but to a separate 150-L oxidation tower (see Fig. 2). The hold tank contains ~10 L of 5 wt% $CaSO_4$ for pH adjustment. A stream of slurry in the hold tank is also drawn to the forced oxidation tower to allow the circulation pump to run smoothly. Slurry gravimetrically overflows to the slurry hold tank where pH is adjusted before it is sent back to the spray tower. The oxidation tower is sparged with air at a constant rate of ~45 L/min to promote the conversion of SO_3^{2-} to SO_4^{2-}. The pH of the slurry is adjusted by adding reagent-grade calcium carbonate ($CaCO_3$) into the hold tank. The addition is metered through a feedback control loop from the hold tank. The pH of the slurry in the hold tank is 5.7 to 6.4. The slurry temperature is maintained at 47±2°C.

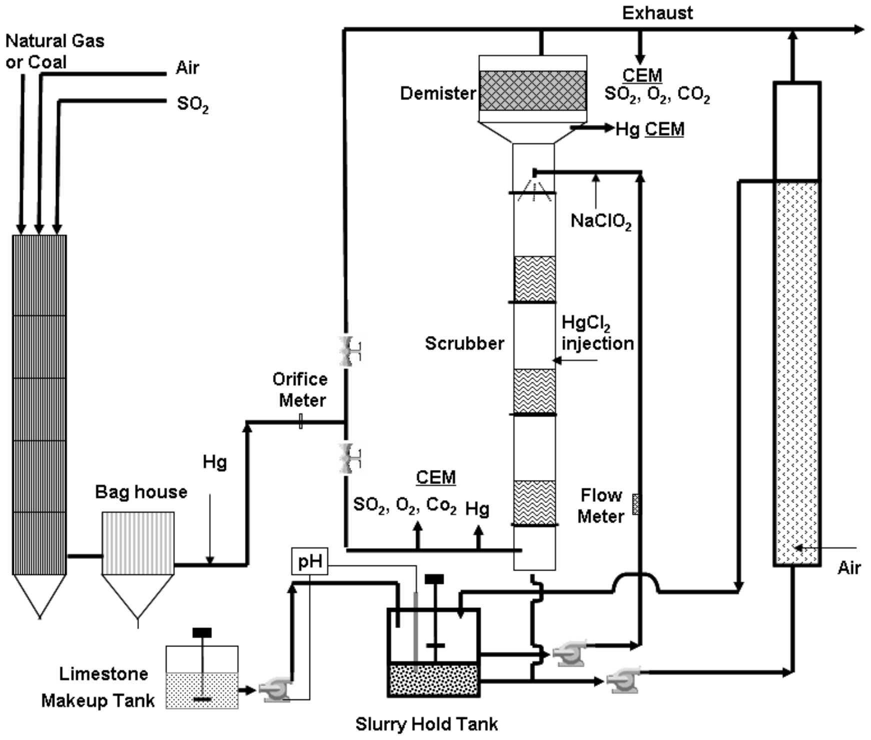

Fig. 2. Schema of the pilot-scale set up
Rys. 2. Schemat instalacji pilotowej

3. Results and discussion

3.1. Initial bench-scale screening tests

Generally, wet flue gas desulphurization scrubbers are designed for SO_2 capture but, theoretically, wet scrubbers can also remove insoluble NO and Hg^0 when NO and Hg^0 undergo oxidation to soluble form as NO_2 (or higher oxides) and Hg^{2+}, respectively. This process requiresthe addition of a soluble, effective oxidant to the scrubber. Therefore, a series of water soluble oxidants were initially examined in order to identify the most promising scrubber additive in these experiments.

Oxidants were injected simultaneuosly with 10% calcium carbonate slurry ($CaCO_3$). The initial screening test results for these oxidants are presented in Fig. 3. Initial results showed that only potassium permanganate ($KMnO_4$), sodium chlorite ($NaClO_2$), sodium hypochlorite (NaOCl) and calcium hypochlorite ($Ca(OCl)_2$ showed significant Hg removal – 100%, 95%, 100% and 56%, respectively. $NaClO_2$, $KMnO_4$ and NaOCl showed encouraging NO oxidation (62%, 34% and 14%, respectively) and NO_x (as NO_2) absorption (36%, 33% and 10%, respectively). However, sodium chlorite ($NaClO_2$) showed the most promising results. The sodium chlorite concentration was the lowest of all oxidants tested, but its pollutant removal efficiencies were the highest. Therefore, sodium chlorite was chosen for further tests because it was the most promising scrubber additive. Additionally, $NaClO_2$ has been described as a good NO oxidizer and NOx sorbent in the literature [2, 3, 16, 18]. However, the studies for which results were reported were largely conducted with only $NaClO_2$ solution or using a $NaClO_2$/NaOH solution. In order to determine the influence of $NaClO_2$ on pollutant removal under our experimental conditions, a second set of baseline tests were performed with $NaClO_2$ solutions in the absence of $CaCO_3$. The second baseline experiments were performed with $NaClO_2$ concentrations of 0.0025 and 0.0088M in the additive solution (the $NaClO_2$ solution plus a deionized water in place of $CaCO_3$ slurry). The results are presented in Table 1. As reported in Table 1, we obtained promsing results using sodium chlorite as the oxidant and absorbent of NOx, Hg and SO_2. Therefore, additional tests were performed to investigate the use of sodium chlorite further.

Table 1. SO_2, NO, NO_x and Hg removed in the initial baseline tests
Tabela 1. Skuteczność usuwania SO_2, NO, NO_x i Hg w badaniach wstępnych

	SO_2 removal [%]	NO removal [%]	NO_x removal [%]	Hg removal [%]
DI water	24	2	2	0
Limestone slurry (10 wt%)	100	< 2	< 2	0
DI water + 0.0025M ClO_2^-	66	26	19	79
DI water + 0.0088 M ClO_2^-	100	70	38	100

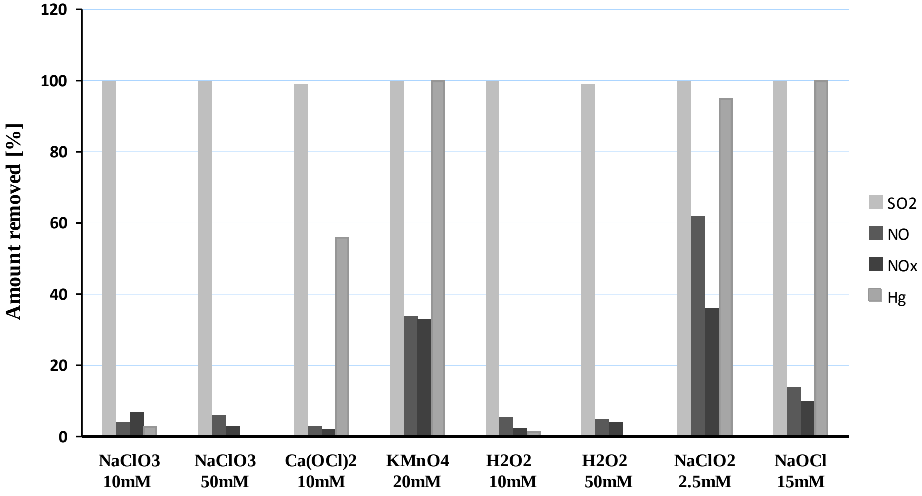

Fig. 3. NO_x, Hg and SO_2 removal in the simulated wet flue gas desulphurization limestone scrubber enhanced by different oxidant additives
Rys. 3. Skuteczność usuwania NO_x, Hg i SO_2 przy zastosowaniu różnych utleniaczy w symulowanym mokrym absorberze odsiarczania spalin zasilanych zawiesiną węglanu wapnia

3.2. Influence of chlorite concentration in the liquor scrubber on multi-pollutant control in the bench- and pilot-scale tests

In order to find the optimum chlorite concentration in the scrubber, a series of experiments with a range of ClO_2^- concentrations was performed at the bench and pilot-scale. The concentration of nitrogen species (nitrate and nitrite anions) in the scrubber effluent was used to calculate nitrogen mass balance. Analysis of Hg and other anions were performed for four selected sodium chlorite concentrations, as well. The influence of the chlorite concentration in the scrubber at the bench and pilot-scale is presented in Fig. 4 and Fig. 5. The initial pollutant concentrations in flue gas were: 206 $\mu g/m^3$ Hg, 200 ppm NO, 1500 ppm SO_2, for the bench-scale experiments, and 1100 ppm SO_2, 220 ppm NO, and 17 $\mu g/m^3$ Hg, for the pilot-scale tests. The concentration of the sodium chlorite additive in the scrubber strongly affected pollutant removal efficiencies. As can be seen in Fig. 4, NO oxidation increased almost linearly by increasing ClO_2^- concentration to 0.005M ClO_2^-, achieving 100%. Further increase of chlorite concentration in the scrubber didn't change the results. NO_x absorption (as NO_2) slightly increased with increasing ClO_2^- concentration in the scrubber liquor, achieving ~40% for 0.005M ClO_2^- to ~ 60% for 0,025 M. Anion analysis showed that nitrogen species (nitrate and nitrite) were consistent with the scrubbing NO_2 from the gas. Hg removal in the bench-scale scrubber was also strongly affected by chlorite concentration (Fig. 4). Hg was oxidized and removed completely at 0.003M chlorite concentration and increasing chlorite further didn't change the results.

Similar experiments were conducted at the pilot-scale. It was observed that a low chlorite concentration in the scrubber (as low as those in a bench-scale) did not work well under the pilot-scale testing conditions. Significant Hg reduction was not observed until the injecting sodium chlorite concentration was increased to 1.62M, as is shown in Fig. 5.

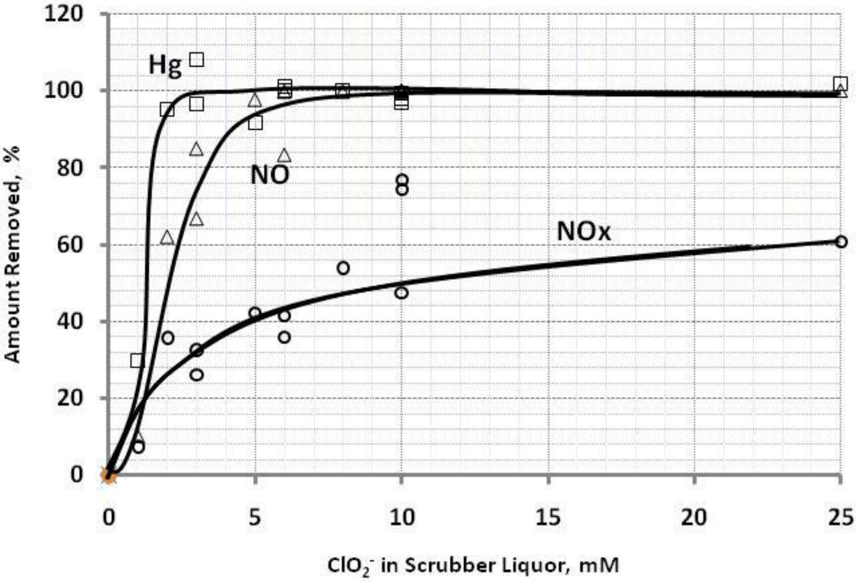

Fig. 4. Effect of oxidant additive concentration in the scrubber on multi-pollutant capture in bench-scale experiments
Rys. 4. Skuteczność usuwania zanieczyszczeń w zależności od stężenia utleniacza w absorberze w skali laboratoryjnej

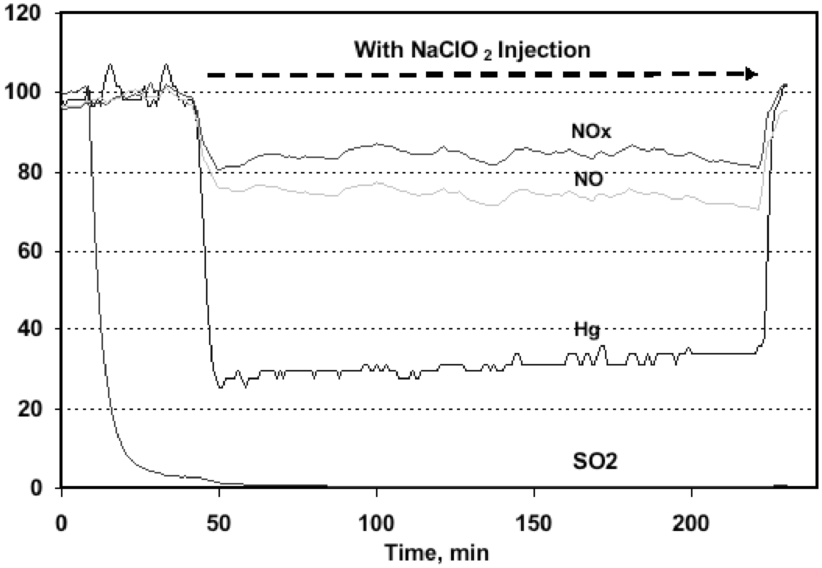

Fig. 5. Multi-pollutant capture across the wet scrubber in the pilot-scale experiment
Rys. 5. Skuteczność usuwania zanieczyszczeń w zintegrowanym absorberze w skali pilotowej

As it is demonstrated, an average Hg removal ~70% was achieved immediately after chlorite solution was sprayed into scrubber. NO and NOx removal efficiencies were 30% and 15% respectively, in that conditions. These initial pilot-scale results indicate that a multipollutant control of Hg, NO_x and SO_2 across a wet scrubber is feasible.

There are many possible reactions possible beetwen NO, NO_x, Hg SO_2 and $NaClO_2$ [2, 3, 10]. There may be different chemical mechanism present in a multi-polluant scrubber depending on the conditons of process, but the likey products of reactions are: NO_2^-(aq), NO_3^-(aq), Hg^{2+}(aq), SO_3^-(aq), SO_4^-(aq), Cl^-(aq), ClO^-(aq), ClO_2^-(aq), ClO_3^-(aq) and possible NO(g), NO_2(g). Detailed mechanisms depend on the pH of the slurry is presented in [14].

Generally, at low pH, NO and Hg^0 are oxidized to NO_2 and Hg^{2+} in the liquid and this creates conditions that promote absorption.NO_2, which is much more soluable than NO, and Hg^{2+}, which is much more soluable than Hg^0, solubizes and reacts in liquid slurry to form nitrites (NO_2^-), nitrates (NO_3^-) and soluble forms of Hg (mainly- $HgCl_2$, $Hg(NO_3)_2$). These potential reactions pathways of NO-$NaClO_2$ are presented in reactions (a) – (e).

$$2NO + ClO_2^- \rightarrow 2NO_2 + Cl^- \qquad (a)$$

$$NO + ClO_2^- \rightarrow NO_2 + ClO^- \qquad (b)$$

$$4NO_2 + ClO_2^- + 4OH^- \rightarrow 4NO_3^- + Cl^- + 2H_2O \qquad (c)$$

$$2NO_2 + ClO_2^- + 2OH^- \rightarrow 2NO_3^- + ClO^- + H_2O \qquad (d)$$

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \qquad (e)$$

Hg may react with $NaClO_2$ solution in the following way (reactions (f) and (g)):

$$Hg^0 + ClO_2^- + 2H_2O \rightarrow 2Hg^{2+} + 4OH^- + Cl^- \qquad (f)$$

$$Hg^0 + 4HNO_3 \rightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O \qquad (g)$$

SO_2 can react very quickly with calcium carbonate slurry, as in convencional flue gas desulphurization scrubber (create $CaCO_3$ and $CaSO_4$), but can also react (to some extent) with chlorite according to reaction (h):

$$2SO_2 + ClO_2^- + 2H_2O \rightarrow H_2SO_4 + Cl^- \qquad (h)$$

Reaction (h) is not a desirable reaction, because it can negatively affect the overal performance of the process. Decreasing chlorite consumption by SO_2 was the subject of subsequent research soon to be published.

The final products of reactions NO–$NaClO_2$ are NO_2^- or NO_3^- ions, which are retained in the scrubber, or NO_2(g) unreacted, which exists the flue gas with any unreacted NO(g). A mass balance from the measurement of total nitrite, nitrate and mercury in the scrubber effluent was mostly consistent with the gas phase assessment. Only the mercury mass balance in bench-scale tests tends to overestimate the amount removed, to an extent, in some cases. This was likely due to analytical difficulties in measuring such small concentrations.

Pilot-scale tests also showed good mass balance, moreover, it was discovered that most Hg captured in the scrubber slurry was found in the liquid phase of the scrubbing liquor. The mercury mass balances, measured and calculated, are presented in Fig. 6. As is shown in Fig. 6, the estimated Hg agreed well with the measured.

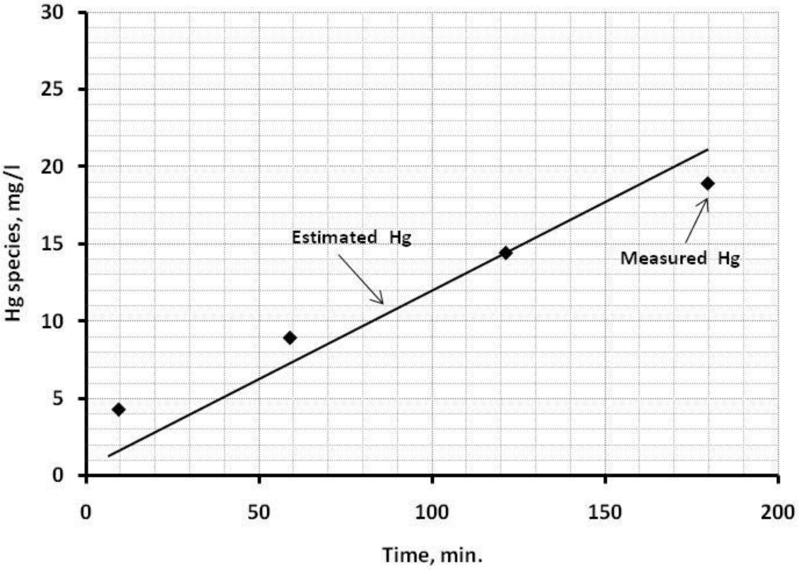

Fig. 6. Amount of aqueous mercury in the scrubber
Rys. 6. Zawartość rtęci w fazie ciekłej absorbera

3.3. Influence of SO_2 in flue gas on multi-pollutant control

A series of experiments evaluating the influence of the SO_2 concentration in flue gas and the pH of the scrubber liquor was performed in bench and pilot-scale tests. The SO_2 concentration varied from 0 to 2500 ppm. These values represent the extreme ranges of what might be seen in the flue gas of a coal-fired power plant. The results are presented in Fig. 7 and Fig. 8. As it is shown, the concentration of SO_2 strongly affected Hg, NO and NO_x removal efficiencies in bench and pilot-scale experiments.

It was demonstrated that a lack of SO_2 in flue gases caused a sharp decrease of Hg removal and was ~80% in a bench-scale experiments and up to ~20% in pilot-scale. The presence of SO_2 at 500 ppm in the flue gas caused complete Hg removal. One hundred percent Hg removal was achieved when

SO_2 concentrations were in the range of 500 to 2000 ppm. The percent removal decreased slightly when SO_2 reached 2500 ppm in bench-scale tests. NO and NO_x followed a similar pattern to Hg in a bench-scale experiments. NO oxidation achieved ~50% and NO_x ~20% when SO_2 was not present in the flue gas. The addition of 500ppm SO_2 promoted NO removal to 100% and the absorption of NOx increased to ~50%, as well. The amount of NO and NO_x removed remained constant when SO_2 varied between 500÷2000 ppm. Further increasing SO_2 concentration decrease NO and NO_x removals to ~80% and ~40%, respectively.

The tests were also conducted in the pilot-scale scrubber (Figs 7 and 8). Hg removal was ~65% and was steady for 500 and 1100 ppm SO_2, it then decresed to ~50% when SO_2 increased to 2000 ppm for 1.62M chlorite in the slurry. When the chlorite concentration in the slurry is lowered (0.8M), Hg removal efficiency decreases quickly (from ~55% when SO_2 was 550 ppm to ~10% for SO_2 2000 ppm) with increasing SO_2 concentration. In both bench- and pilot cases, high levels of SO_2 dramatically lowered Hg oxidation.

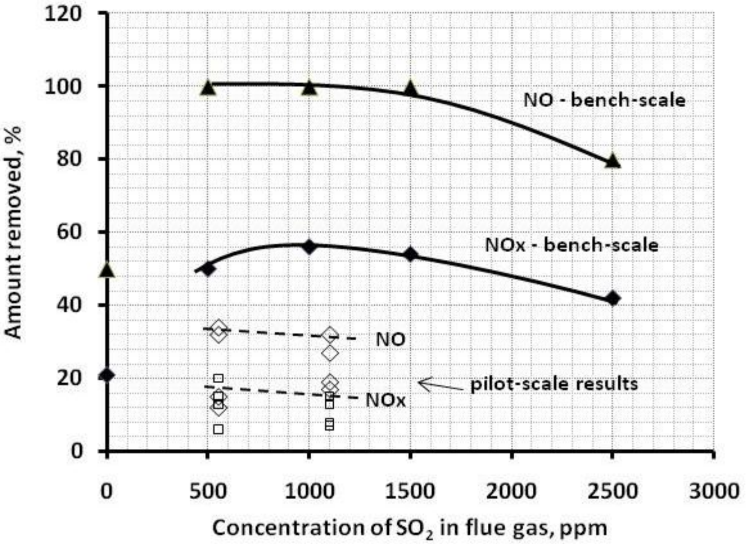

Fig. 7. Effect of SO_2 in flue gas on NO/NO_x capture in the bench- and pilot-scale tests

Rys. 7. Skuteczność usuwania NO/NO_x w zależności od stężenia SO_2 w gazach spalinowych skali laboratoryjnej i pilotowej

NO and NO_x capture were tested in the range of 550÷1100 ppm SO_2 in a pilot scale. It was found that changing SO_2 concentration (in that range) did not affect the results. As is shown in Fig. 8, NO and NO_x removal (for both chlorite concentrations) did not change significantly in the range 550÷1100 ppm SO_2.

As it was demonstrated, the presence of SO_2 is important to Hg and NO removals and a small amount of SO_2 in the flue gas is essential to achieve complete Hg and NO removals. However, a high concentration of SO_2 decreases pollutant removal efficiencies, probably depleting $NaClO_2$ and deactivating the Hg-$NaClO_2$ reaction.

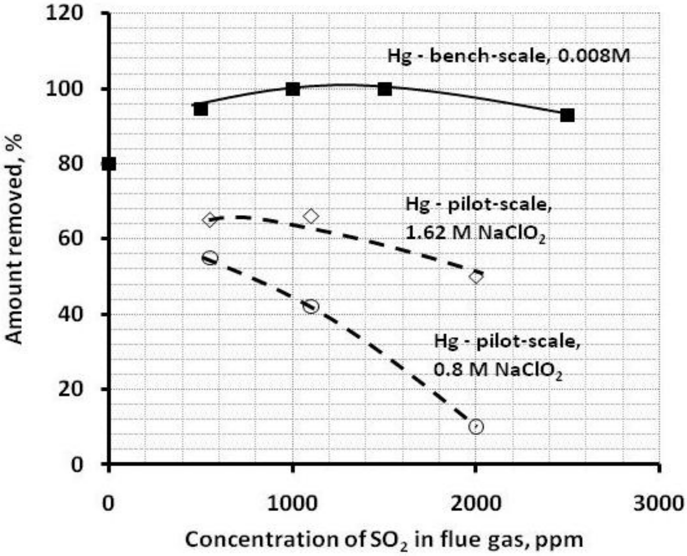

Fig. 8. Effect of SO_2 in flue gas on Hg capture in the bench- and pilot-scale tests
Rys. 8. Skuteczność usuwania Hg w zależności od stężenia SO_2 w gazach spalinowych skali laboratoryjnej i pilotowej

3.4. Influence of pH in the wet scrubber on multi-pollutant control

A series of experiments was performed in a range of acidic to alkaline solutions to find the optimum values of pH with respect to simultaneous removal of NO_x, Hg and SO_2. This parameter is important when practical applications and the place of oxidant injection are considered. The pH in the scrubber/channel or before/after scubber may strongly varies. Resutlts from experiments showing the effect of pH on the removal process are presented in Fig. 9. It was found that acidic solution is favorable for NO and Hg^0 removal, achieving ~100% NO and ~90% Hg removal in in bench-scale tests. Increasing the pH decreases the oxidative power. Increasing pH above 6.5 caused decreasing NO, Hg and NO_x removal (~50%, ~60% and ~36% respectively) at 9.0 pH. However, it was found that the percentage of total NO_2 captured in the scrubber (from everything present in the scrubber) was higher when compared to acidic pH. This statement is supported by results from other experiments that are presented in the following paper [14]. There is a different NO removal mechanism in acidic and alkaline solution as supported by detailed ion analysis and presented in detail in [14], as well.

Pilot-scale experiment was performed under two pH values – 5.7 and 6.4. The tests showed that there were no significant changes in pollutants removals when varying pH between these two values (Fig. 9). However, a higher pH (7.4), when SO_2 was not present in the flue gas, caused significant a decrease in Hg removal – less than 20% of the Hg was removed by the scrubber in pilot-scale test (see Fig. 9).

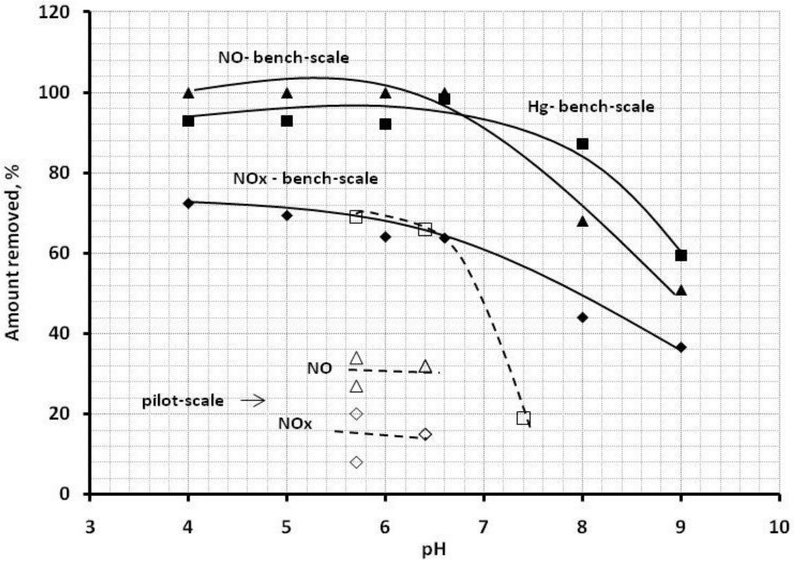

Fig. 9. Effect of pH in the scrubber on multi-pollutant capture in the bench- and pilot-scale tests

Rys. 9. Skuteczność usuwania zanieczyszczeń w zależności od pH absorbera w skali laboratoryjnej i pilotowej

Bench-scale experiments using a wide range of pH showed that sodium chlorite is a suitable additive for the simultaneous removals of SO_2 and NO and Hg from the flue gas in the pH range of 4÷6.5 and do not require tight pH control. However, if we need higher NO_x absorption, further improvements are necessary because oxidation processes – NO/Hg^0 and NO_x (as NO_2) absorption, need different conditions. Increasing of $NO_x(NO_2)$ absorption is the subject of further research.

4. Conclusions

Sodium chloride was effective additive in a limestone wet scrubber for the simultaneous removals of NO_x Hg and SO_2. Bench-scale experiments showed nearly complete removals of SO_2, Hg and NO and ~50% NO_x (as NO_2) with low levels of chlorite additive into the scrubbing liquor (~0.005M). An excess supply of additive did not improve NO and Hg removal but slightly improved NOx absorption (to ~60% at 0.025M ClO_2^-). Initial pilot-scale results showed lower but still promissing pollutants removal (~70% Hg, ~30% NO, ~15% NOx). It was found that presence of SO_2 is one of the most critical parameters in respect to Hg and NO removals. It was discovered that a lack of SO_2 in a flue gas negativelly affected Hg and NO removals, causing a dramatic decrease in Hg and NO removal in a bench- and pilot-scale experiments. A small amount of SO_2 in the flue gas is essential to achieve complete Hg and NO removals, but if the SO_2 concentrations is too high, it will decrease pollutants removal efficiencies by depleting $NaClO_2$ and deactivating the Hg-$NaClO_2$ – NO-$NaClO_2$ reactions. Experiments with with wide range of pH showed that sodium chlorite is a suitable additive for the simultaneous removals of SO_2 and NO and Hg from the flue gas in a wide pH range (4÷7.0) and that a tight pH control is not required. However, if we need higher NO_x absorption, further improvements are necessary. Increasing of NO_x removal is the subject of future research.

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Badania laboratoryjne i pilotowe nad zintegrowanym oczyszczaniem spalin z dwutlenku siarki, tlenków azotu i rtęci w układach mokrego odsiarczania spalin

Streszczenie

Redukcja emisji dwutlenku siarki (SO_2), tlenków azotu (NO_x), a także rtęci (Hg) jest istotnym problemem ochrony środowiska. Związane jest to z coraz większą świadomością społeczeństwa o zagrożeniach, jakie niesie ze sobą zanieczyszczenie powietrza, troską o zdrowie oraz z dyrektywami unijnymi jak LCP-2001/80/EC, IED w Europie czy CATR w USA, które wymuszają dodatkowe ograniczenia tychże substancji [5, 6, 19]. Powyższe

aspekty motywują do rozwoju tzw. „czystych technologii węglowych", a także technologii ograniczania emisji zanieczyszczeń z kotłów opalanych węglem. Dyrektywa LCP (Large Combustion Plants Directive) nakłada obowiązek oczyszczenia spalin z dużych obiektów energetycznych do poziomu 200 mg NO_x/Nm^3 i 200 mg SO_2/Nm^3 po 2016 r. [7]. Dyrektywa IED (Industrial Emissions Directive) dotycząca emisji przemysłowych, zaostrza jeszcze powyższe limity po roku 2016 (2020 w Polsce) [19]. Dyrektywy te praktycznie nakładają obowiązek modernizacji lub zainstalowania nowoczesnych, wysokosprawnych instalacji odsiarczania i odazotowania na większość polskich elektrowni [15]. Dlatego też, oprócz dalszego rozwoju komercyjnie dostępnych technologii takich jak SCR (Selektywna Redukcja Katalityczna) i SNCR (Nieselektywna Redukcja Katalityczna), opracowywane są również inne techniki oczyszczania spalin z NO_x, do których należą m.in. techniki „multipollutant" (zintegrowanego oczyszczania), które są przedmiotem badań autorów niniejszej publikacji.

W prezentowanych badaniach podjęto próbę opracowania metody redukcji emisji SO_2, NO_x i Hg w układach mokrego odsiarczania spalin. W artykule przedstawiono wyniki badań laboratoryjnych i pilotowych. Celem pracy było uzyskanie wysokich, redukcji emisji zanieczyszczeń oraz zbadanie i ustalenie optymalnych warunków prowadzenia procesu (stężenie jonów ClO_2^- w zawiesinie sorpcyjnej, wpływ SO_2 i NO_x w gazach spalinowych oraz pH cieczy sorpcyjnej). Badania przeprowadzono w skali laboratoryjnej i pilotowej na gazach Symulujących składem gazy spalinowe z procesu spalania węgla. Proces usuwania zanieczyszczeń przebiegał w absorberach symulujących mokre absorbery odsiarczania spalin, zasilanych wodną zawiesiną węglanu wapnia. Badania pilotowe przeprowadzono w absorberze trzykolumnowym z wieżą natleniającą. Badania laboratoryjne wykazały bardzo wysoką skuteczność usuwania SO_2, NO_x i Hg ze spalin, przy niskim stężeniu ClO_2^- w zawiesinie sorpcyjnej (0.005M). Hg i NO zostały całkowicie usunięte ze spalin, natomiast absorpcja NO_x (w postaci NO_2) wynosiła ok. 50%. Większe stężenia ClO_2^- w zawiesinie nie wpływały na poprawę efektywności procesu. Wstępne badania pilotowe wykazały niższe, lecz obiecujące skuteczności usuwania zanieczyszczeń (~70% Hg, ~30% NO, ~15% NO_x). Wykazano, że obecność SO_2 w spalinach jest bardzo istotnym parametrem wpływających na skuteczność usuwania NO_x (NO i NO_2) i Hg. Z kolei brak SO_2 w spalinach powodował drastyczny spadek skuteczności usuwania zanieczyszczeń. Wykazano, że niewielka ilość SO_2 w gazach spalinowych jest niezbędna do uzyskania wysokich redukcji stężeń NO_x (NO i NO_2) i Hg, natomiast zbyt wysokie stężenie SO_2 w spalinach powoduje dezaktywację reakcji Hg-$NaClO_2$-NO-$NaClO_2$ i wpływa negatywnie na sam proces oczyszczania. Udowodniono również, że chloryn sodu jest skutecznym związkiem utleniającym NO i Hg^0 w absorberze w zakresie pH 4.0÷7.0.