Polish J. of Environ. Stud. Vol. 19, No. 6 (2010), 1255-1262

Original Research

Absorption of NO_x, SO_2, and Mercury in a Simulated Additive-Enhanced Wet Flue Gas Desulphurization Scrubber

Renata Krzyżyńska[1,2]*, Yongxin Zhao[3], Nick Hutson[1]**

[1]U.S. Environmental Protection Agency, Office of Research and Development,
Research Triangle Park, NC 27711 USA
[2]Faculty of Environmental Engineering, Wroclaw University of Technology,
Wybrzeze Wyspianskiego 27, 50-379 Wrocław, Poland
[3]Arcadis G&M, Inc, Durham, NC 27713 USA

Received: 19 December 2009
Accepted: 30 March 2010

Abstract

Bench- and pilot-scale studies were conducted on the simultaneous removals of SO_2, NO_x, and mercury (both Hg^0 and Hg^{2+}) from coal combustion flue gas using a limestone-based wet flue gas desulfurization (FGD) scrubber. The wet scrubber performance for multi-pollutant control was significantly enhanced with the introduction of an oxidizing additive – sodium chlorite ($NaClO_2$). Parametric studies investigating the effects of flue gas components (e.g., SO_2, NO), temperature, and oxidant addition rate were completed with the bench- and pilot-scale experimental facilities. Various process configurations were examined to optimize the addition of sodium chlorite. Additional tests were also performed to better understand the chemistry of the oxidation and subsequent capture of the pollutants of interest.

Keywords: multi-pollutant, sulfur dioxide, nitrogen oxides, mercury, flue gas

Introduction

Coal combustion is the primary means of power generation in Poland, providing 59% of the total energy supply [1]. It is anticipated that coal will continue to be the dominating energy source for at least the next 20 years [2]. However, the combustion of fossil fuels causes the release of various pollutants such as SO_2, NO_x, and mercury. Their harmful effects on human health and the environment are well known and documented. For example, sulfur dioxide (SO_2) is the major contributor to the precipitation of acid rain, and nitrogen oxides (NO_x) are a precursor of smog by reacting with volatile organic compounds. The increasing concern about mercury arises from its damage to nerves and kidneys [29]. Therefore, developing and implementing "clean coal technologies" to control these hazardous air pollutant emissions from flue gas to meet United States Clean Air Interstate Rule (CAIR) and European Directive 2001/80/EC emission standards is critical [3, 5]. Current emission standards by Directive 2001/80/EC demand that electric utilities control emissions of NO_x and SO_2 below 200 mg/m^3 beginning in 2016. Although the EU has not issued any mercury-related rules, it is expected that eventually mercury emissions will be caped in a similar way as in the United States [4]. Despite this, currently available FGD technologies, in particular limestone-based wet scrubbers, are able to scrub SO_2 as high as ~95%. The primary deNO_x techniques, such as low nitrogen burner (LNB), are not efficient enough to meet new emission criteria in the US CAIR

---

*e-mail: renata.krzyzynska@pwr.wroc.pl
**e-mail: hutson.nick@epa.gov

[3] and European Union directive [5]. The installation of post-combustion NO_x control devices, such as selective catalytic reduction (SCR), is one way to meet the stringent emission standards. It is anticipated that deployment of SCR systems will continuously increase and ~50% of the coal-firing plants will have SCR installed by 2020 [6]. Notwithstanding, the increasing price of ammonia (which is synthesized from natural gas) [32] might throw a roadblock to the wide deployment of SCR systems.

Mercury is a component of coal and during the combustion process is released as Hg^0 (elemental mercury) [33, 34]. Mercury reacts with different flue gas components and exists in three different forms in flue gases: elemental Hg^0 (elemental) and Hg^{2+} (oxidized form, e.g. $HgCl_2$), and Hg in particulates (Hg_p) [33, 34]. The elemental Hg^0 does not dissolve in water and is not usually captured in air pollutant control devices (APCD), while the Hg in particulates is captured upstream of particulate control devices (e.g. electrostatic precipitator (ESP) or fabric filter (FF)). The oxidized form dissolves in water and can be captured with water spray or in a flue gas desulphurization (FGD) unit [33, 34]. Wet-FGD scrubbers have the potential to provide a high level of mercury control because of their substantial gas-liquid mass transfer and the high solubility of most oxidized mercury compounds (such as $HgCl_2$). This co-benefit control is only effective for flue gas streams containing oxidized forms of mercury, because the elemental form is not soluble and tends to pass through the wet scrubber [33, 34].

Mercury, well known for its toxic properties regarding human health and the environment, should be removed from flue gas [21]. A variety of technologies are being developed to control mercury emissions from coal-fired power plants, including sorbent injection, catalyst oxidation, flue gas or coal additives, combustion modification, barrier discharges, and ultraviolet radiation [22-24]. Co-benefit application of SCR in combination with wet scrubber without any additional capital investment is the most favorable solution [30]. However, challenges still exist due to the potential deactivation of SCR catalysts by fly ash [31].

Worldwide research efforts have shed light on individual SO_2, NO_x, and mercury emission reductions [8-20, 27]. Technological approaches for multipollutant control differ dramatically, and some have gone beyond the co-benefit endeavor of current air pollutant control devices. For example, ReACT technology (ammonia and activated carbon) and ECO (plasma) has achieved commercial application [8, 9]. However, their application to the coal-fired power plant commands additional equipment and investment. One concept recently introduced is the multi-pollutant control where SO_2, NO_x, and other pollutants are simultaneously controlled in a single air pollutant control device. Apparently, the multipollutant control across wet FGD is an option. Following the wide deployment of wet-FGD scrubbers in response to CAIR and the EU Directive, researching and developing a process where the wet scrubber is capable of providing simultaneous multi-pollutant (SO_2, NO_x, and Hg) control is attractive.

The U.S. Argonne National Laboratory recently claimed that an integrated multi-pollutant approach through the wet FGD system can outperform current emission control strategies in the following ways:
(1) optimization of resource and energy,
(2) lower capital and operating costs, and
(3) operational reliability [7].

In this approach, one multi-pollutant control technology can be realized by introducing additives to the wet scubber where NO and elemental Hg can be oxidized and scrubbed. This type of approach is also most attractive for small or medium boilers. In addition, extending this application to the cement or waste treatement industry would be interesting as well.

A lot of work has been performed in an effort to remove NO in the sodium chlorite solution by oxidation of NO to NO_2 or elevated states of oxides [11, 14-16, 26-28]. NO in general has a low solubility and it is extremely difficult to achieve removal across a wet scrubber without it being converted into soluble matter, e.g. NO_2 [25]. As such, the success of NO_x removal from flue gas when a wet scrubber is utilized should involve oxidation of NO to NO_2 and then scrubbed in a liquid slurry. When oxidant is added to the wet scrubber, it also has the potential to oxidize elemental mercury, which is not water soluble. The efforts presented in this paper are, therefore, to illustrate the role played by sodium chlorite in promoting NO_x and Hg scrubbing across a wet limestone scrubber system.

Bench-Scale Demonstration

The performance of $NaClO_2$ in promoting multi-pollutant control was first investigated with bench-scale tests. The bench-scale experimental apparatus, Fig. 1, made use of a flow-through gas-liquid impinger to simulate a wet FGD scrubber. The system included a gas blending system for the makeup of synthetic flue gas, a flow-through gas-liquid impinger, and an online gas analysis system for measurement of the flue gas stream constituents. Slurry was pumped through the impinger, being maintained at a constant slurry level through overflow mechanics. The scrubber was operated at 55ºC by immersing the scrubber into a constant temperature water bath. Sodium chlorite ($NaClO_2$) and calcium carbonate were mixed prior to being introduced to the scrubber through separate ports. The constant addition of $NaClO_2$ was manipulated via weight losses in the beaker. The alkali solution addition rate was monitored via the weight gain from the overflow of the scrubber. Simulated flue gas was introduced to the experimental system from gas cylinders. The gas mix was comprised of 11% CO_2, 8% O_2, 1,500 ppmv SO_2, 200 ppmv NO, 206 $\mu g/m^3$ Hg^0, and balanced with N_2. The flow of the simulated flue gas was maintained at 2 L/min (STP). Elemental mercury vapor was supplied from a VICI Metronics Dynacalibrator permeation oven, maintained at 100ºC and transported by N_2. The high level of mercury was necessary to meet the required sensitivity of the mercury analyzer. Prior to analysis, the sampling gas passes through an ice cooler and a

Table 1. Summary of Experimental Conditions in Bench-Scale Experiments.

Experimental conditions	Value	Remark
SO_2	0-2,500 ppm	SO_2 in nitrogen
NO	0-470 ppm	NO in nitrogen
CO_2	11 vol %	Compressed CO_2
O_2	8 vol %	Compressed air (N_2/O_2)
N_2	balance	Compressed N_2
Hg^0	206 μg/m^3	H^0 permeation tube at 100ºC
Total flue gas flow	2 L/min	Std conditions, 1 atm and 20ºC
Scrubber slurry solids wt %	10 wt %	Alkali and oxidant solutions combined
Oxidant concentration	varied	Sodium chlorite
Scrubber temperature	55ºC	Controlled by water bath

Nafion dryer, where moisture is removed. Hg^0 vapor was measured using a continuous cold vapor atomic absorption (CVAA) analyzer (BUCK model 400A). The interference of SO_2 to mercury analyzer was determined and corrected together with the downstream SO_2 analyzer. The SO_2 species were measured using a continuous SO_2 fluorescence analyzer (model 100AH, Advanced Pollution Instrumentation, Inc.). The NO_x species were measured using a continuous chemiluminescence NO_x analyzer (model 200AH, Advanced Pollution Instrumentation, Inc.).

Slurry was feeding simultaneuosly with the oxidizer to the impinger until it started to overflow. A magnetic stirrer was used to promote the mixing of slurry. The agitation was maintained at a constant speed throughout all runs. Flue gas was then introduced to the impinger and the test was continued for 60 minutes. Fresh $NaClO_2/CaCO_3$ was added at a constant rate during the scrubbing period. The scrubber effluent was collected every 10 minutes toward the end of the test. Collected samples were immediately weighed, and ice quenched to minimize potential oxidation reactions. Filtrate from samples was then analyzed as soon as practically possible for chloride, chlorite, chlorate, sulfate, nitrate, and nitrite concentrations with ion chromatography (IC) using EPA reference method 300.0.

Simultaneous Removal of SO_2, NO_x, and Hg

Simultaneous removal of SO_2, NO_x, and Hg was tested at 55ºC by using SO_2, NO, and Hg concentrations of 1,500 ppm, 200 ppm, and 206 μg/m^3, respectively. NO_x and Hg removal efficiencies and resulting NO_3^-, NO_2^-, and Hg^{2+} ion concentrations in the liquor are presented in Figs. 3 and 4. SO_2 removal efficiency was complete before the addition of $NaClO_2$, This information is not presented in the figures for clarity. Data show that NO was completely oxidized into NO_2 when $NaClO_2$ concentration reached 5.0 mM. NO_2 scrubbing increased along with increasing $NaClO_2$ addition, ranging from 40% at 5.0 mM $NaClO_2$ up to 60% at 25

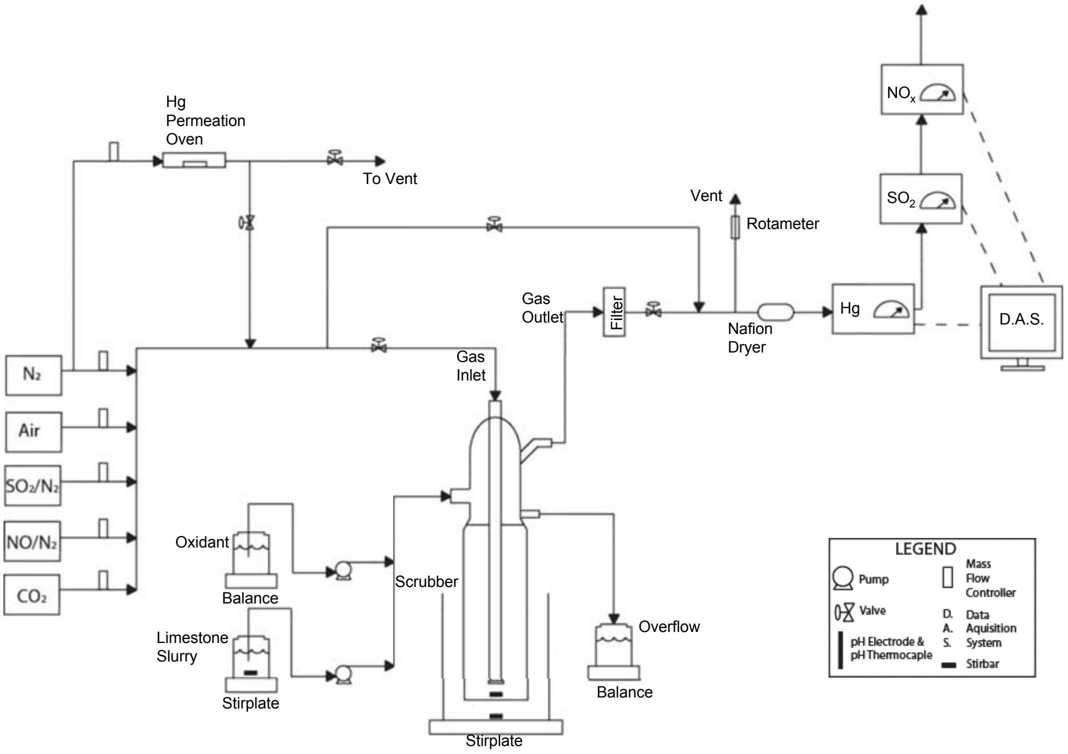

Fig. 1. Bench-scale experimental schema.

mM $NaClO_2$. The corresponding nitrogen species (nitrite and nitrate) in the slurry was consistent with the scrubbing of the NO_2 from the gas stream. The amount of Hg^0 removed as a function of chlorite concentration is shown in Fig. 4. Mercury was completely removed with the addition of 3.0 mM $NaClO_2$. The mass balance in some cases was not well closed, most likely due to analytical challenges in measuring low levels of Hg^{2+} concentration.

Effect of SO_2 Concentration

The effect of SO_2 concentration on the simultaneous removal of NO_x, SO_2, and Hg at 55ºC was performed at initial NO of 200 ppm, Hg^0 of 206 μg/m³, $NaClO_2$ of 8.0 mM, and $CaCO_3$ of 10% (wt %) solid slurry. The SO_2 concentration varied from 0 to 2,500 ppm. These values represent the extreme ranges of what might be seen in the flue gas of coal-fired utilities.

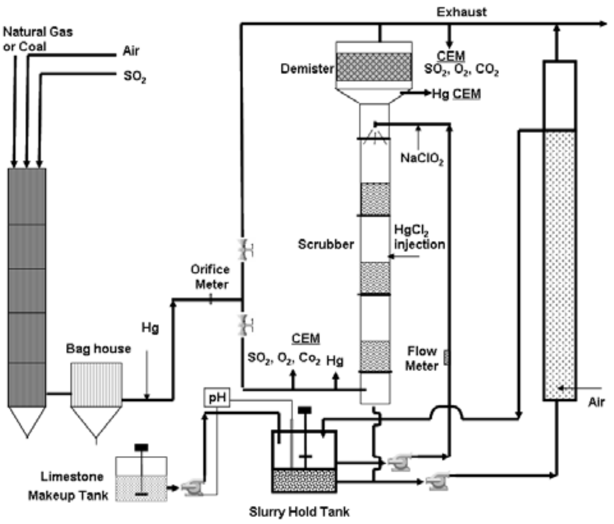

Fig. 2. Schematic of the pilot-scale wet scrubber system.

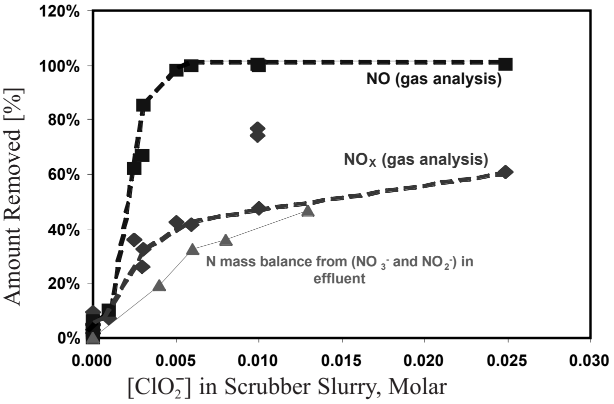

Fig. 3. Amount of NO and NO_x removed as a function of chlorite concentration in the $CaCO_3$ slurry. The inlet concentration of NO was 200 ppm. The initial SO_2 concentration was 1,500 ppm.

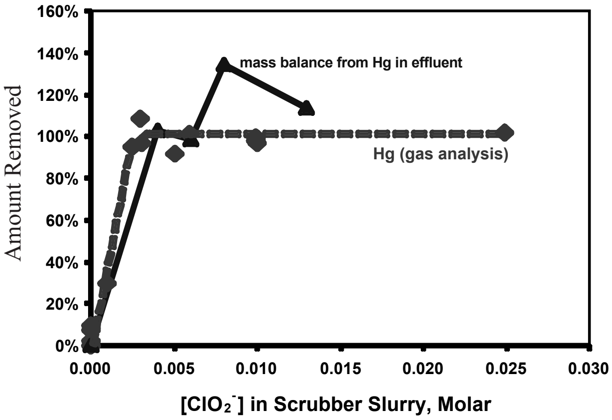

Fig. 4. Amount of Hg^0 removed as a function of chlorite concentration in the $CaCO_3$ slurry. The inlet concentration of NO was 200 ppm. The initial SO_2 concentration was 1,500 ppm.

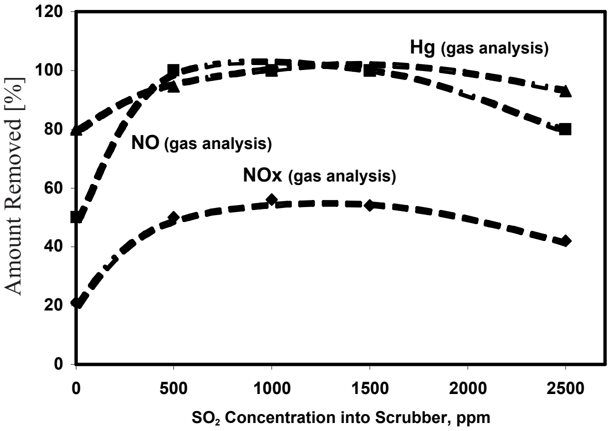

Fig. 5. Amount of NO, NO_x, and Hg removed as a function of varying concentration of SO_2 in the entering gas. The entering concentration of $NaClO_2$ added was 8 mM. NO concentration in entering gas was 200 ppm.

The lack of SO_2 in flue gas causes a dramatic decrease in Hg, NO, and NO_x removal efficiency (Fig. 5). In this case, only 50% NO removal (oxidized) and 80% of mercury removal was observed. NO_2 absorption was also low (~20%). This phenomenon is most likely related to the pH of the medium, where high levels of pH are unfavorable for Hg^0 and NO oxidation. An addition of a low-SO_2 concentration of 500 ppm to flue gas had rendered a 100% removal of NO (oxidation) and mercury on the opposite side of the spectrum due to the lack of SO_2. The same level of NO and Hg removal was continued in the presence of SO_2 and was consistent until it reached 2,500 ppm where NO removal decreased to ~75%. The NO_x (as NO_2) scrubbing followed a similar pattern with lower scrubbing with no SO_2 addition, an increase with SO_2 addition, and then a decline at the highest SO_2 addition.

Effect of NO Concentration

The effect of varying NO concentration on NO_x, SO_2, and Hg removals at 55ºC was performed under the following conditions: SO_2 =1,500 ppm, Hg^0 = 206 μg/m³, $NaClO_2$ = 8.0 mM, $CaCO_3$ = 10% (wt %), and the range of NO varying from 0 to 470 ppm. The results presented in Fig. 6 illustrate that the absence of NO in flue gas affects mercury oxidation to a certain degree. At 0 ppm NO, the Hg oxidation and removal was approximately 82% and approached 100% with increasing NO concentrations. NO was completely oxidized when NO concentrations were present from 100-300 ppm, and decreased to approximately 65% at 470 ppm NO. The NO_x (as NO_2) scrubbing followed a similar pattern as NO.

Effect of Temperature

Increasing temperature accelerates the reaction rate, but decreases gas solubility in the liquid. Additional experiments were conducted to identify the effects of varying temperature. The temperatures that were evaluated ranged from room temperature to 65ºC. Test conditions also included the following: 8.0 mM $NaClO_2$, 10% (wt) solid slurry, 200 ppm NO, 1,500 ppm SO_2, and 206 μg/m³ Hg. The oxidation and removal percentage for NO, and Hg holds the same across the testing range of temperature (Fig. 8). Temperature in the range of 25-65ºC had a negligible effect on pollutant removal efficiences in these experimental conditions.

Pilot-Scale Demonstration

Tests were also conducted utilizing a pilot-scale scrubber system as shown in Fig. 2. The system was consistently operated in the forced oxidation mode. Simulated flue gas was generated from a down-fired cylindrical furnace, known as the innovative furnace reactor (IFR). Although it is capable of burning coal, the IFR is typically fired with natural gas at approximately 158,000 kJ/h. 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 doped from gas cylinders to achieve the desired flue gas concentrations. Similar to the Hg generated for bench-scale tests, gaseous Hg^0 was produced in a permeation oven (VICI Metronics Dynacalibrator) and was transported by air into the duct before the scrubber.

The spray tower where SO_2, NO_x, and Hg are scrubbed consists of three turbulent contact absorbers (10-cm in diameter). Each absorber is 92-cm in length, and contains plastic hollow balls (2-cm in diameter) to promote intimate contact between flue gas and scrubbing slurry. The effluent slurry from the spray tower was not discharged to the underlying slurry hold tank, but rather to a discrete forced oxidation tower. A flow of ~45 L/min air was sparged to the bottom of the forced oxidation tower to oxidize SO_3^{2-} into SO_4^{2-}. The slurry overflowed back to a small hold tank positioned below the scrubbing tower. Slurry in the hold tank was subsequently delivered back to the top of the spray

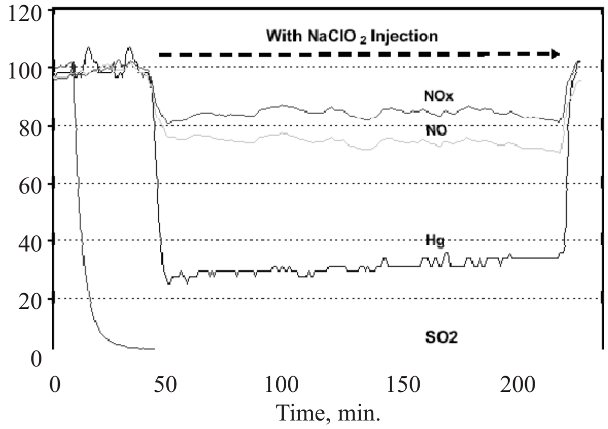

Fig. 7. Effect of nominal 1.62 M $NaClO_2$ injection at 5 mL/min. (hold tank slurry pH=6.4).

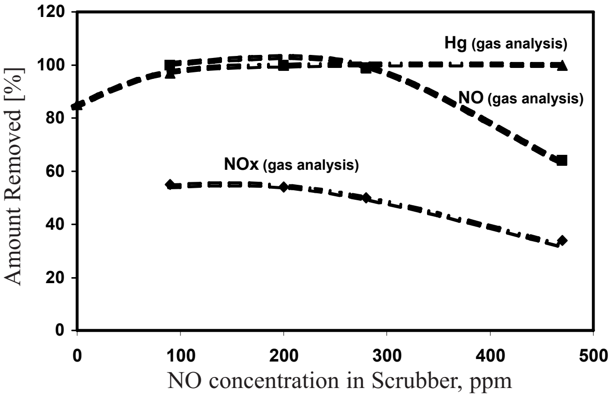

Fig. 6. Amount of NO, NO_x, and Hg removed as a function of varying concentration of NO in the entering gas. The entering concentration of $NaClO_2$ added was 8 mM. SO_2 concentration in entering gas was 1,500 ppm.

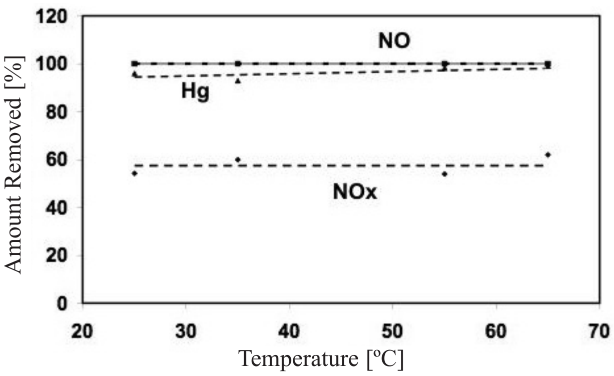

Fig. 8. Amount of NO, NO_x and Hg removed as a function of temperature in the scrubber. The entering concentration of $NaClO_2$ added was 8 mM. The inlet concentration of NO was 200 ppm. $SO_2$2 concentration – 1,500 ppm.

Table 2. Typical test conditions of the wet scrubber in the pilot-scale experiments.

Experimental Condition	Parameter
Flue gas flow rate, L/min	850
Inlet flue gas SO_2 concentration, ppm	1,100±100
Inlet flue gas NO_x concentration, ppm	220±20
Flue gas O_2 concentration, %	7-8
Flue gas CO_2 concentration, %	6-7
Hold tank slurry volume, L	10
Hold tank pH	6.4
Slurry recirculation rate to scrubber, L/min	2.2±0.2
Slurry recirculation rate to oxidation tower, L/min	30
Hold tank slurry temperature, ºC	46±2
Hg feed concentration, μg/Nm^3	17±2
Hg^{2+} feed rate, μg/min	15±0.4
$NaClO_2$ addition concentration, M	1.62
Air sparged to the forced oxidation tower, L/min	45
Diameter of forced oxidation tower, cm	25.4

tower. $NaClO_2$ solution was added approximately 0.3-m away from the spray nozzle to reduce its potential consumption by SO_3^{2-} ions.

The hold tank contained ~10 L of 5% (wt.) ($CaSO_4$) slurry during testing. The slurry was agitated to keep the solids uniformly suspended. The pH of the slurry was maintained by the addition of calcium carbonate ($CaCO_3$), which is regulated through a feedback control loop from the limestone makeup tank. The concentrations of SO_2, NO_x, O_2, and CO_2, etc., were continuously monitored at both the scrubber inlet and outlet using continuous emission monitoring systems (CEMs). Measurements of Hg^0 were performed using ultraviolet (UV) spectrometers (Seefelder-Hg 3000) at the scrubber inlet and outlet and at the outlet of the forced oxidation tower. The NO_x species were measured using a continuous chemiluminescence NO_x analyzer (model 200EH, Teledyne Technologies Company). The SO_2 species were measured using a continous Fluorescence SO_2 analyzer (model 100 AH, Advanced Pollution Instrumentation, Inc.) The test conditions for demonstration are shown in Table 2.

The resulting observation is illustrated in Fig. 7. Once the operating conditions were stabilized, 1.62 M $NaClO_2$ and 3 μg/mL $HgCl_2$ were continuously fed into the scrubber at 5 mL/min. The addition of $HgCl_2$ was to increase the accumulation of $HgCl_2$ in the wet scrubber system to identify the potential re-emissions. As demonstrated in Fig. 7, where the exiting flue gas dimensionless concentrations vs. time are plotted, flue gas Hg, NO, and NO_x across the scrubber rapidly declined following the $NaClO_2$ injection. At steady state, ~65% of the Hg was removed from the flue gas. Although NO and NO_x across the scrubber declined as well, these pollutants decreased at a diminishing rate. In Fig. 7, ~32% of NO was oxidized into NO_x, and only ~15% of total NO_x was removal across the wet scrubber system.

It appears that the multi-pollutant control across a wet scrubber system demands the addition of $NaClO_2$, which is critical for initial Hg reduction. Efforts continued by varying the $NaClO_2$ addition concentration. The results showed that the extent of scrubbed Hg increases with increasing chlorite addition in the slurry, ranging from ~40% at 0.81 M $NaClO_2$ up to ~70% at 1.62 M $NaClO_2$. However, the scrubbing for NO with pilot-scale wet scrubber still ranged from 15 to 30% for selected $NaClO_2$ injection rates. The addition rate of $NaClO_2$ had little effect on the scrubbing of NO_x. It was observed that there is a lower pollutant removal efficiency in pilot-scale test than in the bench-scale. Further research will focus on optimization of process conditions in order to increase pollutants removal efficiencies in that type of multi-pollutant scrubber.

Chemistry in the Multi-Pollutant Wet Scrubber

According to the literature [14-16, 26-28] there are many possible reactions among the flue gas components and $NaClO_2$. The possible chemical reactions that may occur in a multi-pollutant wet scrubber fed by sodium chlorite and slurry of calcium carbonate are presented below (reactions 1-14).

$$4NO + ClO_2^- + 4OH^- \rightarrow 4NO_2^- + Cl^- + 2H_2O \tag{1}$$

$$2NO + ClO_2^- + 2OH^- \rightarrow 2NO_2^- + ClO^- + H_2O \tag{2}$$

$$2NO_2^- + ClO_2^- \rightarrow 2NO_3^- + Cl^- \tag{3}$$

$$2NO + ClO_2^- \rightarrow 2NO_2 + Cl^- \tag{4}$$

$$NO + ClO_2^- \rightarrow NO_2 + ClO^- \tag{5}$$

$$4NO_2 + ClO_2^- + 4OH^- \rightarrow 4NO_3^- + Cl^- + 2H_2O \tag{6}$$

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \tag{7}$$

$$5SO_2 + 2ClO_2^- + 6H_2O \rightarrow 5H_2SO_4 + 2HCl \tag{8}$$

$$SO_2 + H_2O \rightarrow 2H^+ + SO_3^{2-} \tag{9}$$

$$2H^+ + SO_3^{2-} + CaCO_3 \rightarrow CaSO_3 + CO_2 + H_2O \tag{10}$$

$$CaSO_3 + \tfrac{1}{2}O_2 \rightarrow CaSO_4 \tag{11}$$

$$2CaSO_3 + ClO_2^- \rightarrow 2CaSO_4 + Cl^- \tag{12}$$

$$2Hg + ClO_2^- + 2H_2O \rightarrow 2Hg^{2+} + 4OH^- + Cl^- \tag{13}$$

$$Hg + 4HNO_3 \rightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O \tag{14}$$

Analysis of experimental results further suggests that pH is of great importance for Hg oxidation as reflected in reaction (13). By removing OH from the scrubber, or maintaining a relatively low pH (<7.0), Hg can be effectively oxidized. The effect of pH has just been studied and will be published soon in another paper.

Conclusions

Our research demonstrated that sodium chlorite is an effective additive for the simultaneous removal of SO$_2$, NO$_x$, and Hg in wet scrubber simulators fed by limestone slurry in bench- and pilot-scale systems.

All bench-scale experiments resulted in SO$_2$ removal efficiency near 100%. Small additions of chlorite as 5.0 mM resulted in nearly complete oxidation and removal of the NO. The NO$_x$ (NO$_2$) removal increased with increasing chlorite addition, ranging from 40% at 5.0 mM NaClO$_2$ up to 60% at 25 mM NaClO$_2$ in the added slurry. Mercury removal efficiency was complete at 3.0 mM concentration of chlorite. Experiments with different concentrations of NO and SO$_2$ showed that the oxidizer is less effective when there is no SO$_2$ and NO present in the flue gas. Mercury oxidation and subsequent removal was 80% when SO$_2$ was not present. A similar pattern was observed for NO, where 50% of NO oxidation and only 20% of NO$_x$ (NO$_2$) was removed in the case of no SO$_2$ present in the simulated flue gas. These lower oxidation and removal efficiencies are likely connected with higher pH in the scrubber when acid gas is not present. Lack of NO in flue gas also caused decreasing mercury oxidation and removal. Elemental mercury reacts with chlorite in flue gas, but can also react quickly with nitric acid. Where no NO is present in the flue gas, there is no HNO$_3$, suggesting that the reaction with nitric acid may have a slight contribution to the overall oxidation of Hg°. This effect is unlikely a bulk effect, because the scrubber liquor did not change significantly. NO oxidation was complete when the range of initial NO concentation in the flue gas varied from 100 to 300 ppm. At 470 ppm of initial NO concentration in flue gas – NO oxidation decreased to about 65%. NO$_x$ (NO$_2$) absorption was by average about 50% of the NO oxidation in all experiments where SO$_2$ and NO were present. Temperature in the range of 25-65ºC did not have a significant effect on pollutant removal efficiencies.

The wet limestone scrubber used in the pilot-scale experiments was operated in forced oxidation mode to treat a simulated flue gas doped with variable amounts of SO$_2$ and nitric oxide (NO). Test results showed that the additive, sodium chlorite (NaClO$_2$), is effective in increasing the amount of Hg$_{total}$ captured in the scrubber and also is effective at increasing the removal of NO$_x$, but to a lesser extent. Apparently, for Hg and NO removals, the addition rate of NaClO$_2$ is of utmost importance. The extent of scrubbed Hg increases with increasing chlorite addition in the slurry, ranging from about 40% at 0.81 M NaClO$_2$ up to about 70% at 1.62 M NaClO$_2$. For NO, the scrubbing was less efficient, ranging from 15-30% for the selected NaClO$_2$ injection rates. The addition rate of NaClO$_2$ had little effect on the scrubbing of NO$_x$.

The initial pilot test confirmed also that under forced oxidation operating mode, NaClO$_2$ was effective for multi-pollutant controls of Hg and NO.

Further research will focus on optimizing process conditions in order to increase pollutant removal efficiencies, mainly of NO$_x$.

Acknowledgements

This work was performed at the U.S. EPA and supported by the Office of Research and Development (ORD). Renata Krzyzynska is an Assistant Professor at Wrocław University of Technology and was appointed to the Postdoctoral Research Program at the National Risk Management Research Laboratory in Research Triangle Park, NC, administered by the Oak Ridge Institute for Science and Education (ORISE) through an Interagency Agreement (BW89938167) between the U.S. Department of Energy (DOE) and the U.S. EPA. Dr. Yongxin Zhao is a Research Engineer with Arcadis U.S., an on-site contractor to EPA/ORD in Research Triangle Park. Dr. Nick D. Hutson is a chemical engineer at the U.S. EPA in Research Triangle Park. Mention of trade names of commercial products and companies does not constitute endorsement or recommendation for use.

References

1. KAVOURIDISA K., KOUKOUZAS N. Coal and sustainable energy supply challenges and barriers. Energy Policy, 36, **2008**.
2. U.S. Department of Energy, International Energy Outlook, report DOE/EIA-0484(2009), May **2009**.
3. EPA Clean Air Interstate Rule (CAIR) can be found at www.epa.gov/cair
4. EPA Clean Air Mercury Rule (CAMR) can be found at www.epa.gov/mercuryrule/
5. Directive 2001/80/WE (LCP) of the European Parliament and of the Council of 23 October 2001 on the limitation of emission of certain pollutants into air from large combustion plants.
6. ZHAO L. L., ROCHELLE G. T. Mercury Absorption in Aqueous Oxidants Catalyzed by Mercury(II). Ind. Eng. Chem. Res., **37**, 380, **1998**.
7. ELLISON W. Chemical process techniques for simultaneous NO$_x$ removal in existing FGD installations, DOE/NETL 2003 Conference on Selective Catalytic Reduction and Non-Catalytic Reduction for NO$_x$ Control, October, **2003**.
8. DENE C., GILBERT J., JACKSON K., MIYAGAWA S. ReACT Process Demonstration at Valmy Generating Station, Proceedings of the the Power Plant Air Pollutant Control "MEGA" Symposium, Baltimore, MD, paper **123**, August 25-28, **2008**.
9. BOYLE P. D. Multi-Pollutant Control Technology for Coal-Fired Power Plants, Proceedings of the Clean Coal and Power Conference Washington, DC November 21-22, **2005**.
10. JIN D.S., DESHWAL B.R., PARK Y.S., LEE H. K. Simultaneous Removal of SO$_2$ and NO by Wet Scrubbing Using Aqueous Chlorine Dioxide Solution, Journal of Hazardous Materials, B135, **2006**.
11. CHEN L., HSU C. H., YANG C. L. Oxidation and Absorption of Nitric Oxide in a Packed Tower with Sodium Hypochlorite Aqueous Solutions. Environ. Prog. 24, **2005**.

12. CHU H., CHIEN T.W., LI S.Y. Simultaneous absorption of SO_2 and NO from flue gas with $KMnO_4$/NaOH solutions, The Science of The Total Environment, **257**, (1-3), **2001**.
13. MYERS E. B., OVERCAMP T. J. Hydrogen Peroxide Scrubber for the Control of Nitrogen Oxides. EnViron. Eng. Sci. 19, **2002**.
14. CHIEN T. W., CHU H., LI Y. C. Absorption Kinetics of Nitrogen Oxides Using Sodium Chlorite Solutions in Twin Spray Columns. Water, Air, Soil Pollut. 166, **2005**.
15. LEE H. K., DESHWAL B. R., YOO K. S. Simultaneous Removal of SO_2 and NO by Sodium Chlorite Solution in Wetted-Wall Column. Korean J. Chem. Eng., **22**, (2), **2005**.
16. DESHWAL B. R., LEE S. H., JUNG J. H., SHON B. H., LEE H. K. DESHWAL Study on the Removal of NO_x from Simulated Flue Gas Using Acidic $NaClO_2$ Solution, Journal of Environmental Sciences, **20**, (1), **2008**.
17. ELLISON W. Chemical Process Design Alternatives to Gain Simultaneous NO_x Removal in Scrubbers, POWER-GEN International, Las Vegas, NV, December 9-11, **2003**.
18. SUCHECKI T.T., RACHWAŁ T. Simultaneous Control of SO_2 and NO_x by the Chelate Method, Zeszyty Naukowe Uniwersytetu w Wuppertalu, **2002**.
19. CHMIELEWSKI A.G., TYMIŃSKI B., PAWELEC A. Removal of NO_x and SO_2 by electron beam process, Ekologia, **6**, 33, **2005**.
20. KORELL J., SEIFERT H., PAUR H.-R., ANDERSSON S., BOLIN P. Flue Gas Cleaning with the MercOx Process, Chemical Engineering & Technology, **26**, (7), 2003.
21. SLOSS L. L. Economics of Mercury Control, report of Clean Coal Center and International Energy Agency, **2008**.
22. FEELEY T.J., MURPHY J.T., HOFFMANN J.W., GRANITE E.J., RENNINGER S.A. DOE/NETL's Mercury Control Technology Research Program for Coal-Fired Power Plants, EM, **2003**.
23. GRANITE E.J., PENNLINE H.W., HARGIS R.A. Novel Sorbents for Mercury Removal from Flue Gas, Industrial & Engineering Chemistry Research, 39, **2000**.
24. GRANITE E.J., PENNLINE H.W. Photochemical Removal of Mercury from Flue Gas, Industrial & Engineering Chemistry Research, **41**, 5470, **2002**.
25. CHIRONNA R. J., ALTSHULER B. Chemical Aspects of NO_x Scrubbing. Pollut. Eng., (April), 32, **1999**.
26. SADA E., KUMAZAWA H., KUDO I., KONDO T. Absorption of NO in Aqueous Mixed Solutions of $NaClO_2$ and NaOH. Chem.Eng.Sci., **33**, **1978**.
27. SADA E., KUMAZAWA H., YAMANAKA Y., KUDO I., KONDO T. Absorption of Sulfur Dioxide and Nitric Oxide in Aqueous Mixed Solutions of Sodium Chlorite and Sodium Hydroxide, Journal of Chemical Engineering of Japan, **11**, (4), **1978**.
28. BROGREN C., KARLSSON H. T., BJERLE I. Absorption of NO in an Aqueous Solution of $NaClO_2$. Chem. Eng. Technol. **21**, 61, **1998**.
29. BOOGAARD PETER J., HOUTSMA AUGUS-TINUS A.J., JOURNEE H. LOUIS SITTERT NICO J. VAN Effects of exposure to elemental mercury on the nervous system and the kidneys of workers producing natural gas, Archives of Environmental Health, March 1, **1996**.
30. LEE S.J., LEE C.W., SERRE S.D., ZHAO Y., KARWOWSKI J., HASTINGS T.W. Study of Mercury Oxidation by SCR Catalyst in an Entrained-Flow Reactor under Simulated Prb Conditions. Presented in Air Quality V. **2005**. Arlington, VA.
31. LEE C. W., SERRE S. D., ZHAO Y., LEE S. J., HASTINGS T. W. Mercury Oxidation Promoted by a Selective Catalytic Reduction Catalyst under Simulated Powder River Basin Coal Combustion Conditions, J. of the Air, & Waste Management Association, **58**, 484, **2008**.
32. HUANG W-J. Impact of Rising Natural Gas Prices on U.S. Ammonia Supply, Outlook Report No. (WRS-0702), United States Department of Agriculture, pp. 19 August **2007**.
33. PAVLISH J.H., SONDREAL E.A.,MANN M.D., OLSON E.S., GALBREATH K.C., LAUDAL D.L., BENSON S.B. Status review of mercury control options for coal-fired power plants, Fuel Processing Technology **82**, 89, **2003**.
34. HUTSON N. D. Mercury Capture on Fly Ash and Sorbents: The Effects of Coal Properties and Combustion Conditions, Water, Air & Soil Poll: Focus, **8**, 323, **2008**.