

1. **Names and Surname:** Renata Krzyżyńska

2. **Diplomas, degrees - with the name, place and year of acquisition**

1. **Doctor of Technical Sciences** (Hons) - Department Mechanical and Power Engineering, Wrocław University of Technology, 2006, Ph.D. thesis, entitled "Mercury removal from coal-fired power plants", supervisor: prof. Mieczysław Adam Gostomczyk
2. **Master of Science** (Hons) - Department of Environmental Engineering, Wrocław University of Technology, Wrocław, 1998 r.
3. Postgraduate Diploma in International Relations and Foreign Trade at the University of Economics in Wrocław, Wrocław, 2000 r.

3. **Information on previous employment in scientific/artistic institutions**

- **Since 10.01.2009** – Assistant Professor, Wrocław University of Technology, Department of Environmental Engineering
- **2007 - 2009** – postdoctoral fellowship at the U.S. Environmental Protection Agency (U.S. EPA), Office of Research and Development, National Risk Management Research Laboratory (NRMRL), Air Pollution Prevention and Control Division, Research Triangle Park, North Carolina, USA.
- **2002 - 2006** – PhD student Wrocław University of Technology, Department of Mechanical and Power Engineering.



4. Indication of achievement under art. Paragraph 16.2 of the Act of 14 March 2003y. about Academic Degrees and Title and Degrees and Title in Art (Journal of Laws No 65, item. 595, as amended.)

A) (author / authors, title / titles of publication, year of publication, name of publisher)

- Krzyżyńska Renata, The integrated flue gas cleaning from SO₂, NO_x and Hg in a wet flue gas desulfurization systems. 2012. Publisher: Wroclaw University of Technology, Scientific Papers of the Institute of Environmental Engineering, Wroclaw University of Technology No. 93, Series: Monographs No. 58.

B) Discussion of the scientific / artistic purposes above mentioned work / works and the results, together with a discussion of their possible use.

My research, after obtaining the doctor degree, focused on the modification of the traditional sulfur dioxide (SO₂) absorption process in calcium carbonate (CaCO₃) slurry in such a way that it was possible to remove nitrogen oxides (NO_x), and mercury (Hg) simultaneously in one absorber.

A literature review showed that, despite the publication of numerous papers on the oxidation and absorption of NO_x and/or SO₂ in water solutions of sodium chlorite (NaClO₂), there aren't data on the simultaneous removal of SO₂, NO_x and Hg in the calcium carbonate slurry with chlorite.

Accordingly, there aren't also mechanisms of oxidation and absorption of these pollutants in such absorbers. The aim of my research was to modify the SO₂ absorption process in calcium carbonate slurry, which leads to the simultaneous removal of SO₂, NO_x and Hg. This modification consisted of the oxidation of insoluble NO to soluble form - NO₂ (or higher oxides of nitrogen) and the oxidation of elemental mercury species - Hg⁰ into a soluble form - Hg²⁺ by dosing the oxidizing reagents to the absorber, mainly sodium chlorite.

The purpose of this study was to determine the substantial changes in the process parameters which play important role in the pollutants removal, such as: reagents concentration, the sulfur dioxide concentration in the flue gas, the nitrogen oxides concentration, the pH of the slurry, temperature, the creation of the oxidation and desulfurization zones in the absorption column working under forced oxidation mode, and also determination of the gas-reagent contact time in the absorber.

Another objective of the research was evaluation of unwanted chlorine dioxide and mercury reemissions mercury from the integrated absorber.

Determination of these correlations was necessary to learn and develop SO₂, NO_x and Hg removal mechanisms in the integrated absorber. Understanding and controlling these mechanisms could provide the maximum pollutant removal efficiencies in the absorber.

Research was conducted in the lab-and pilot-scale absorbers simulating wet limestone FGDs. Flue gas was generated from a controlled mixture of cylinder gases and its composition simulating the real flue gas from coal combustion. Mass flow controllers and valves were used to control the flow of the component gases to provide a standard simulated flue gas comprised of approximately 81 vol. % N₂, 11 vol. % CO₂, 8% O₂, 0-2500 ppmv SO₂ (depending on the experiment), 0-470 ppmv NO (depending on the experiment), and 206 µg/m³ Hg⁰. The mercury concentration was a few times greater than is typical for a coal combustion flue gas to accommodate the sensitivity of the mercury analyzer.

The simulated gas was heated to 90°C and the wet scrubber temperature was maintained at 55°C. The reagents were fed at a constant speed and strictly defined concentrations. The total flow of the simulated flue gas was 2 L/min (STP). Pollutants concentration was monitored by a series of continuous gas analyzers and all results were automatically recorded by a data acquisition system every 10 s. The collected effluent samples were filtered and analyzed by Ion Chromatography (IC). Thorough ion analysis allowed performing a mass balance and developing chemical mechanism of the process.

In order to determine the specific research question, six research systems, which were set up and customized for the particular research problem. Laboratory conditions allowed maintaining all process parameters at constant level, except for one – tested. Conducting research this way, it was possible to estimate the rules of the process, which would be practically impossible in a full-scale.

The research showed, that application of water solution of sodium chlorite in the wet limestone scrubbers may be beneficial in NO_x (NO + NO₂ and higher oxides) and Hg (Hg⁰ + Hg²⁺) removal without reducing SO₂ removal efficiency.

The impact of changes was determined in relevant process parameters on the SO₂, NO_x and Hg removal efficiencies. Research showed that pH strongly influences the chemical mechanism in the scrubber and affects the pollutants removal. The highest

pollutants removal efficiencies were achieved at slurry pH below 3.0. However, under such conditions, there is some risk of the chlorine dioxide emission from the absorber, which may escape from the absorber.

However, there wasn't $\text{ClO}_{2(\text{gas})}$ presence after the multipollutant scrubber, because chlorine reacted quickly with other gas components, what detailed ions analysis confirmed.

Higher pH values resulted in a sharp declining of NO and Hg^0 oxidation. The most optimal pH range for the pollutants removal was from 4.0 to 7.0. For these pH values pollutants removal are high and the risk of chlorine dioxide is negligible. Research showed also, that lack of sulphur dioxide in flue gas causes sharp decreasing of NO and Hg removal efficiencies. On the other hand, the low concentrations of sulphur dioxide in flue gas were necessary to remove NO and Hg effectively, because sulphur dioxide naturally decreases slurry pH.

Research showed that pH strongly influences the chemical mechanism in the scrubber. The chemical removal mechanism presence at low and high pHs is different, what affects pollutant removal efficiencies. The detailed chemical mechanism of pollutants removals at different slurry pHs is described in the monograph.

Further studies have shown that the NO concentration in the flue gas affects mainly the mercury removal. The absence of NO in the flue gas affected the amount of mercury oxidation and removal, what was probably connected with lack of nitric acid in the slurry. Research showed that nitric acid might play some role in the mercury removal mechanism. Changing the temperature in the integrated absorber in the range of 25–65°C did not significantly impact the pollutants removal efficiencies.

Research results showed, that the location at which the oxidant is injected is important (before, into or after the wet scrubber) and the final removal efficiency depends on the chemical conditions of the system, which can vary greatly between different flue gas cleaning systems.

The results showed that the application of sodium chlorite solution after wet scrubber for flue gas desulphurization is beneficial for very low concentrations of chlorite (less than 3.0 mM $n_{\text{NO}}/n_{\text{ClO}_2} \approx 0,8$). For such low concentrations it was possible to obtain the highest amount of NO and Hg oxidized. This may positively influence the overall

economy of the process. In this configuration the mercury was removed entirely at the lowest concentration of sodium chlorite used. For example, in the experiment in which the concentration of sodium chlorite was 0.7 mM ($n_{\text{NO}}/n_{\text{ClO}_2} \cong 3,5$) almost complete mercury removal, with 40% NO and 25% NO_x, was achieved.

For comparable concentrations of chlorite ions, in the system where calcium carbonate slurry was injected together with chlorite, resulted in only 10 percent mercury removal efficiency (with 8% NO and 5% of the NO_x). Similar results were achieved also in the system, when the chlorite was applied before the wet absorber. Such high pollutants removal efficiency in the system in which chlorite solution was injected after the wet scrubber, at such low chlorite ions concentration, was associated with a small amount of sulfur dioxide and sulfates(IV) and bisulfates(IV), which may consume chlorite ions intended for the NO and Hg⁰ oxidation.

These results indicate that applying the oxidizer after the wet scrubber could control mercury perfectly or could be used as an additional step in removing the mercury and NO_x from the gases after other NO_x control facilities using a very low concentration of oxidant.

Research results showed, that the highest NO_x absorption (above 90% at 8.0 mM ClO₂⁻ ($n_{\text{NO}}/n_{\text{ClO}_2} \cong 0.3$)) was achieved when the chlorite was injected before the wet scrubber. Such a high NO_x absorption and other pollutants removal efficiency was connected with the partial decomposition of sodium chlorite in the acidic medium to chlorine dioxide, which quickly reacts with the other flue gas components. This solution is the most effective but most likely associated with the highest, among the tested solutions, investment costs. These costs would include for example: anticorrosive reactor, increased consumption of sodium chlorite and chlorine dioxide detectors. Theoretically, the most economical and the most practical solution would be the integrated absorber, where calcium carbonate slurry was injected together with sodium chlorite. Theoretically, the integrated scrubber would be the least expensive solution in a practical application, when consider only capital cost, because no other reactors or space would be required. However, the operating cost might be higher than in other configurations because of higher sodium chlorite usage. Moreover, results showed that it was difficult to achieve a NO_x removal efficiency greater than ~50-60% in that case.

Further studies were performed in an absorption column with forced oxidation mode at laboratory scale. The oxidation and desulfurization zones were created in the absorption column. The oxidation zones provided appropriate conditions for NaClO_2 -Hg/NO reactions and minimized undesirable reactions involving $\text{SO}_2/\text{SO}_3^{2-}/\text{HSO}_3^-$.

The results showed that the injection of an aqueous solution of sodium chlorite above desulfurization zone is much more favorable option for removing NO/ NO_x and Hg than simultaneous application of $\text{CaCO}_3/\text{NaClO}_2$ slurry to one zone. This relationship didn't change with the extension of gas-reagent contact time. This effect is due to reduced concentration of SO_2 and $\text{SO}_3^{2-}/\text{HSO}_3^-$ ions, which may partially consume sodium chlorite. Through the creation of oxidation zone high pollutants removal efficiency can be achieved at a lower concentration of dosed reagent. Furthermore, studies have also shown that the sulfur dioxide is not the main parameter influencing the increased consumption of sodium chlorite, but $\text{SO}_3^{2-}/\text{HSO}_3^-$ ions, which are formed in the desulphurization process. The aim of the further research was to increase the scale and verification of laboratory results in a pilot plant (50,000 Nm^3/h) simulating spray absorber working under forced oxidation mode. In order to facilitate slurry turbulence and improve reagent-gas contact time a perforated plastic balls were applied in the absorption column.

Studies have shown that, it's possible to create an integrated absorber in which SO_2 , NO_x , and Hg can be effectively removed. Pollutants removal efficiency depends on many parameters, of which the most important are: the concentration of chlorite, the place of its injection, the concentration of $\text{SO}_3^{2-}/\text{HSO}_3^-$ ions, and SO_2 in flue gas, which is consistent with previous studies conducted in a smaller scale.

It was found that the main factor in competing with sodium chlorite is not gaseous SO_2 , but $\text{SO}_3^{2-}/\text{HSO}_3^-$ ions what is also consistent with studies conducted in a smaller scale.

Therefore, to achieve higher pollutants removal efficiency it is necessary to reduce the concentration of $\text{SO}_3^{2-}/\text{HSO}_3^-$ ions in the slurry. Therefore, the aeration of the slurry leaving the absorber should be applied (oxidation tower was used in the experiments), so $\text{SO}_3^{2-}/\text{HSO}_3^-$ ions are oxidized to sulphates, making them neutral for sodium chlorite.

The research results showed that, there is no mercury reemission from the absorber. Preliminary simulation studies have shown that the mercury captured in the

absorber is strongly linked and its reduction process may be more complicated than in the classic absorber, resulting in zero or negligible mercury reemission.

Author's original contribution to the development of the field of environmental engineering is:

- Developing the method for simultaneous removal of SO₂, NO_x, and Hg in wet flue gas desulphurization systems fed by calcium carbonate and sodium chlorite slurry.
- Determining the substantial changes in the process parameters which play important role in the pollutants removal, such as: reagents concentration, the sulfur dioxide concentration in the flue gas, the nitrogen oxides concentration, the pH of the slurry, temperature, the creation of the oxidation and desulfurization zones in the absorption column working under forced oxidation mode, and also determination of the gas-reagent contact time in the absorber.
- Developing SO₂, NO_x, and Hg removal mechanisms in the integrated absorber, determination chlorine dioxide and mercury reemission from the integrated absorber.
- Creating a real basis for the design work on the integrated method of SO₂, NO_x, and Hg removal. It should be emphasized that in a case of practical application, it's not required the construction of new installation, but only modernization of existing limestone wet scrubbers.

5) Discussion of the other research achievements

In 2002, I started PhD studies at Wroclaw University of Technology Faculty of Mechanical and Energy under the supervision of prof. Mieczyslaw A. Gostomczyk. The main area of my interest was reduction of mercury emissions from coal-fired boilers. Most of the research at that time was related to the mercury removal from flue gas using activated carbon impregnated with sulfur or bromine. My research were related to estimating mercury emissions and distribution of mercury in coal, and the various elements of the flue gas cleaning system, and then develop the method

of mercury removal from dry and semi-dry flue gas desulfurization scrubbers equipped with a fabric filter.

Research was conducted on the real flue gas from the boiler OP-430 in a pilot plant WAWO-2 in heat and power plant - Kogeneracja Wroclaw S.A. The mercury removal process was based on the mercury oxidation in the gas phase and its adsorption on the fabric filter cake. The role of the oxidizing substances held: ozone, hydrogen peroxide, sodium hypochlorite, calcium hypochlorite, while the sorbent used was dry calcium hydroxide, which showed the highest percentage of sorption of oxidized mercury. Research showed complete mercury removal from flue gas.

The study was mainly focused on the removal of mercury from flue gas, however nitric oxide concentrations were measured too. Studies showed that it is possible also the partial nitrogen oxides removal from the flue gas. The concentrations of mercury in coal flue gas (Hg^0 , Hg^{2+} and Hg_p) and ash (from electrostatic precipitator and slag) were estimated. The characteristics of coals, ashes and balance of mercury were also conducted.

The PhD thesis entitled: "Mercury removal from coal-fired power plants" was defended with distinction.

The developed solution for mercury removal with oxides of nitrogen and sulfur in dry and semi-dry flue gas desulphurization systems, equipped with a fabric filter, was reported for the innovation competition and was nominated as one of the ten the most innovative solutions for environmental protection in Europe in the competition: "European Environmental Press Award 2005 " - Environmental Innovation for Europe", organized by the European Environmental Press (EEP) in collaboration with the French Trade Fair for Environmental Protection (POLLUTEC) and the European Federation of the Association of Environmental Professionals (EFAEP). The solution was described in 13 journals in Europe.

In 2006 I gave a presentation on one of the largest and most prestigious industry conferences in the U.S., "Power Plant Air Pollutant Control" MEGA "Symposium" in Baltimore. After the presentation, representatives of the U.S. EPA offered me applying for postdoctoral fellowships.

In April 2007, I started a two-year postdoctoral fellowship in one of the world's top research centers in the field of environmental protection belonging to the U.S. EPA in Research Triangle Park, North Carolina, USA. A postdoctoral scholar

("postdoc") in the U.S. EPA, according to "The Scientist", ranks for years among the top places for a postdoc in the world.

The aim of my research was to develop a method of integrated removal of SO₂, NO_x and Hg in wet flue gas desulfurization systems, in the most popular type of absorber in the world. During the stay, I had unlimited access to the testing equipment, as well as flexibility in the formulation of research problems and solve them through the experiments. Formal care of my fellowship in the U.S. EPA fulfilled dr Nick D. Hutson.

The interesting research experience, in which I was involved, was research in Gadsden power plant, Alabama, USA, in December 2007, to which I was invited by the US-Australian company Indigo Technologies and Southern Company (the largest energy producer in the United States). The main goal of research was the cooling and humidifying flue gas and enhancing the removal of sulfur dioxide, nitrogen oxides, mercury and polycyclic aromatic hydrocarbons in the dry flue gas desulphurization system equipped with a particulate matter separator with using hydrogen peroxide (H₂O₂) and calcium hydroxide (Ca(OH)₂).

Another research experience in industrial scale was a study conducted in the Dolna Odra power plant in 2009, to which I was invited by prof. Gostomczyk and company Energotechnika-Energorozruch S.A. Research was related to enhance the process of nitrogen oxides removing in full-scale wet desulphurization system with using hydrogen peroxide.

Summarizing my publishing achievements in the period after obtaining a doctoral degree, I was the author and co-author of 19 publications in scientific journals, collective works and conference proceedings, one U.S. patent and author of a habilitation monograph. Five published articles are in the Journal Citation Reports (JRC). Total impact factor of published articles in a JRC, in accordance with the year of publication is 5.634 (5-year: 7.451). Another written publication of pilot experience will be sent to Energy & Fuels in the near future.

My articles have been cited 22 times according to Web of Science database and 25 times according to Scopus (without self-citations).

I presented my research results at national and international conferences in countries such as: USA, Spain, Germany, Hungary and South Africa.

The results of my research, I used to design the absorber, in which sulfur dioxide, nitrogen oxides and mercury can be removed either together or separately

using a method that takes into account the use of reagents / or their mixtures / as: NaClO_2 , NaClO_3 , H_2O_2 , KMnO_4 , $\text{Ca}(\text{OCl})_2$, together with the slurry of calcium hydroxide and oxides, carbonates and bicarbonates of calcium (either alone or mixed) together or separately, injected with various levels of the absorber (U.S. patent: U.S. 8,012,438).

There are also issues related to the renewable energy and the environment in the area of my interest, and especially the problems of protecting the atmosphere. In the years 2009 – 2011, I participated in the project "Identification of potential and resources of Lower Silesia Region in the science and technology in order to improve the quality of life - indicating the future directions of development. Research based on Foresight methods". The project was co-financed by the European Union. I was a "leader of experts" in the science sector. I actively participated in many meetings, discussions with representatives of the sectors of science, industry, society and administration, preparing the reports and took part in a panel discussion at the project summarizing conference.

Since 2010, I am participating in the construction of a full-scale climatic chamber.

Since 2009, I performed sixteen reviews for following journals: Chemical Engineering Journal, Energy & Fuels, Environmental Progress, Environmental Science & Technology, Fuel, Fuel Processing Technology, Industrial & Engineering Chemistry Research and Journal of the Air & Waste Management Association.

Krzysztof Reneta