

### Author's summary of professional accomplishments

1. Name and surname: **Kazimierz GAJ**
2. Diplomas and scientific degrees:
  - **Master of Science in environmental engineering** – Wrocław University of Technology, Faculty of Sanitary Engineering, specialty: engineering of environmental protection, 1982;
  - **Doctor of Technical Sciences** – Wrocław University of Technology, Environmental Protection Institute, 1992, PhD thesis title: “Biological treatment of selected waste gases using model experimental plant with fluidized bed”.
3. Information on previous employment in scientific institutions:
  - **1982 - 1993** – Wrocław University of Technology, Environmental Protection Institute, technologist, specialist;
  - **1993 - until now** – Wrocław University of Technology (actually Wrocław University of Science and Technology), Faculty of Environmental Engineering, adjunct.
4. Scientific achievement according with Art. 16 par. 2 of the Act of 14 March 2003 concerning the scientific degrees and titles (Journal of Laws No. 65, item 595, with changes):
  - 4.1. Title of the scientific achievement: **“Biogas in air pollution control engineering”** – a series of publications which are all related to the field of mathematical modeling, treatment and monitoring of biogas within engineering and protection of the atmosphere.
  - 4.2. List of above mentioned publication series:
    1. Gaj K., Cybulska-Szulc H., Modelowanie emisji biogazu ze składowisk odpadów komunalnych. Część 1. Podstawy modelowania, analiza wybranych modeli i zakresy stosowanych parametrów [*Modeling of biogas emission from municipal landfill sites. Part 1. Bases of modeling, analyze of the selected models and scopes of their parameters*], 2002, *Chem. Inż. Ekol. [Ecol. Chem. Eng.]*, 9(1), 92-100.
    2. Gaj K., Cybulska-Szulc H., Modelowanie emisji biogazu ze składowisk odpadów komunalnych. Część 2. Algorytm obliczeniowy [*Modeling of biogas emission from municipal landfill sites. Part 2. Mathematical algorithm*], 2002, *Chem. Inż. Ekol. [Ecol. Chem. Eng.]*, 9(2-3), 213-220.
    3. Gaj K., Cybulska-Szulc H., Modelowanie emisji biogazu ze składowisk odpadów komunalnych. Część 3. Weryfikacja modelu w oparciu o badania polowe i jej ocena statystyczna [*Modeling of biogas emission from municipal landfill sites. Part 3. Model verification based on field tests and its statistical evaluation*], 2002, *Chem. Inż. Ekol. [Ecol. Chem. Eng.]*, 9(7), 741-750.
    4. Gaj K., Cybulska-Szulc H., Knop F., Steininger M., Examination of biogas hydrogen sulphide sorption on a layer of activated bog ore, 2008, *Environ. Prot. Eng.*, 34(4), 33-41.
    5. Gaj K., Knop F., Trzepierczyńska I., Technological and environmental issues of biogas combustion at municipal sewage treatment plant, 2009, *Environ. Prot. Eng.*, 35(4), 73-79.

6. Gaj K., Knop F., Cybulska-Szulc H., Badania sezonowej zmienności składu biogazu powstającego w procesie fermentacji osadów ściekowych, w: Oczyszczanie ścieków i przeróbka osadów ściekowych, T.4, red. Sadecka Z. [*Research on the seasonal changeability in the composition of biogas formed during sewage sludge digestion, in: Wastewater treatment and transformation of sewage sludge, vol. 4, Sadecka Z. (ed.)*], 2010, Ofic. Wyd. Uniw. Zielonogórskiego, Zielona Góra, 113-123, ISBN 978-83-7481-337-2; identical in: *Forum Eksploatatora [Forum of Exploiter]*, 2010, 6(51), 70-74.
7. Gaj K., Cybulska-Szulc H., Knop F., Method of simultaneous measurement of total sulphur, chlorine and fluorine content in biogas, 2011, *Environ. Prot. Eng.*, 37(1), 23-30.
8. Zamorska-Wojdyła D., Gaj K., Hołtra A., Sitarska M., Quality evaluation of biogas and selected methods of its analysis, 2012, *Ecol. Chem. Eng. S*, 19(1), 77-87.
9. Gaj K., Cybulska-Szulc H., Time changeability model of the bog ore sorption ability, 2014, *Ecol. Chem. Eng. S*, 21(1), 113-123.
10. Gaj K., Ciołek J., Pakuluk A., Steininger M., Siloksany w biogazie – geneza, zagrożenia, problemy analityczne [*Siloxanes in biogas – origin, hazards and analytical problems*], 2014, *GWITS*, 88(10), 394-397.
11. Gaj K., Pakuluk A., Volatile methyl siloxanes as a potential hazardous air pollutants, 2015, *Pol. J. Environ. Stud.*, 24(3), 937-943.

I evaluate my author's contribution in above mentioned publications as dominant. I am the main initiator and undivided author of the articles concept, formulated research problems and thesis, research programmes and one of the main their performers. I interpreted obtained results and developed conclusions. I am the main or sole author of the manuscripts. My detailed author's contribution I have presented in Appendix No. 3 and co-authors statements – in Appendix No. 4.

#### 4.3. Scientific objective of the above mentioned publications and obtained results with description of their potential applications

In connection with the increasing environmental protection requirements, particularly in the field of air protection and waste management, as well as the EU's policy of reducing the greenhouse effect and promoting renewable and scattered energy sources, the issue of biogas has gained importance in recent years. Progress in the field of biogas technologies required the development of methods for modeling the processes of biogas production and purification, improvement of analytical methodologies to assess its quality and abatement of the adverse effects of certain biogas components and its combustion products to equipment and atmospheric air. These scientific objectives have determined my subject research since 1997.

Initially (1997-2002) my research interests focused on landfill biogas. I conducted research within the university programme of own research (two projects in the field of gas productivity modeling) and within collaboration with municipal economy. The result was determination of: qualitative and quantitative composition of biogas formed in different phases of landfill operation, seasonal variability of biogas composition and seasonal distributions of biogas components' concentrations in ambient air. The

results confirmed literature reports on the presence of carcinogenic compounds from the group of halogenated hydrocarbons in landfill biogas [1], wherein concentration for “Maślice” landfill in Wrocław several times exceeded typical values [2]. I used the obtained set of measurement data to develop a mathematical model of temporal variability of biogas emission [4.2.1 - 4.2.3]. The review and analysis of available models [4.2.1] have shown that they are not representative in the Polish conditions due to inadequate waste group selected for testing (e.g. [3]), the need for specific local data (e.g. [4]) or the lack of consideration phases of the process and differences in the susceptibility of different waste fractions for biochemical decomposition. In [4.2.2] I introduced assumptions, the mathematical form of the model and the algorithm for determining the balancing factor to ensure compatibility between the total, theoretical amount of biogas resulting from the known Tabasaran’s equation and the total amount of biogas obtained for each year of storage, calculated by proposed exponential equations. Comparative calculations, which I performed with the US EPA model [1] gave a similar total amount of the produced biogas; however, the runs of the variations of biogas production showed significant differences. They resulted from the assumptions of the process phases and fractional differentiation of the waste degradation rate constants in the own model. With a large experimental database of ambient air concentrations, the model was validated and refined with own empirical coefficients [4.2.3]. I developed the full model algorithm and its verified form, together with the statistical assessment of the applied method, in the framework of two research projects financed by the Polish State Committee for Scientific Research (KBN): “Development of a computer model of the biogas emission from municipal landfills” (1998) and “Verification of the landfill biogas emission model based on field tests” (2001). The algorithm takes into account the variability of the biogas production with changing parameters such as: storage time, annual amount of landfilled waste, decay time of various waste fractions, organic carbon content and temperature of fermentation. The software developed on the basis of the model enables to design the concept of landfill degassing installation and biogas utilization plant, as well as to forecast the environmental impact of landfills, to which it has been applied many times (for details see Annex 3).

Between 2002 and 2013 I conducted a quarterly research of biogas from sewage sludge digestion process at Wrocław WWTP (WOS). Measurements performed at seven points of biogas transmission and treatment installation included: basic composition ( $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{C}_x\text{H}_y$ ), energetic parameters, density, humidity, content of condensate, dust (including size distribution), silica, oils, hydrogen sulfide, ammonia and the total content of sulfur, chlorine and fluorine compounds. Their aim, in addition to the ongoing control of the fermentation process and biogas treatment as well as the calibration of automation system, was to gather information and recommendations aimed at designing modernization and expansion of WOS. It was carried out in 2010 and consisted of, among others, the change of the so far ineffective biogas desulfurization and drying systems. The results, together with supplementary own research, were the basis of the following scientific purposes accomplished by me:

- discovery of the trends of seasonal changes in the physicochemical parameters of biogas formed from sewage sludge in the long-term time horizon and determination of the relationship between the selected parameters, based on a statistical analysis of the test results [4.2.6, 5],
- intensification and modeling of biogas purification processes [4.2.4, 4.2.9],
- identification of technological and environmental troubles associated with energetic biogas utilization and ways of their minimization [4.2.5],

- development of analytical methodologies for assessing the quality of biogas [4.2.7, 4.2.8, 4.2.10].

Research on biogas from sewage sludge [4.2.6, 5] showed the stability of the basic composition and energy parameters of dry biogas, with their small changes correlated seasonally. They confirmed a variability of CH<sub>4</sub> concentration typical for mesophilic digestive chamber in the range of 60-67% and the total participation of CH<sub>4</sub> with CO<sub>2</sub> within 99,8-99,95%. A proof of a stable methanogenesis was the lack of hydrogen in any of the measurement sessions. Evident seasonal correlation (polynomial of the second degree) occurred in the case of the content of condensate at 0°C and relative humidity of biogas. Significant fluctuations, but without seasonal dependence, were subject to the concentration of sulfur compounds, halides and ammonia, which resulted from the variability in the composition of waste water and unstable operation of biogas purification systems. Atypical was a large variation range of H<sub>2</sub>S concentrations in raw biogas at their relatively low values (average: 42 mg/m<sup>3</sup>, range of variation: 14-364 mg/m<sup>3</sup>). Interesting, due to absence of literature data on that subject, was also a large variation in the share of hydrogen sulfide sulfur in total sulfur (66-98%, an average of 85%).

The results of the research aimed at understanding the causes of technological and environmental troubles associated with biogas combustion in cogeneration units' engines are presented in [4.2.5]. The main reason for the decrease of the system availability was blocking the heat exchanger with deposits. The study included the analysis of the chemical composition of deposits taken from different temperature zones of the exchanger. The test results showed that they consist primarily of sulfates (VI) and iron carbonyls. The silica was not detected, confirming that the two-stage purification of biogas (bog ore/activated carbon) is sufficient to remove the siloxanes. Volatile iron carbonyls are formed in the presence of carbon monoxide, which has been found in the biogas. The source of iron could be sewage sludge and bog ore. The achieved results enabled to put forward the thesis that the main cause of precipitation deposition, in addition to insufficient biogas purification from sulfur and volatile metal compounds, is the periodic exchanger operation at underload conditions, resulting in the formation of lower temperature zones. The fluctuation in a generator load, related to the variability of the demand for biogas and limited possibilities of its storage, cause the temperature in the heat exchanger outlet to vary within a wide range. Periodic temperature drops below the acid dew point of the exhaust gas cause condensation and precipitation of sulfates. The resulting deposits undergo further crystallization and form porous structures which are a good adsorbent for sulfur compounds. Thermal analysis showed excess SO<sub>4</sub><sup>=</sup> ions with respect to the quantity that could be bound by the cations, which supported the idea of sulfuric acid and SO<sub>3</sub> sorption occurring on the deposits. They may be re-released by desorption as a result of temperature increase, as indicated by the presented results of SO<sub>2</sub> emission measurements. At temperature above 500°C, which prevails at the inlet to the heat exchanger, partial thermal decomposition of sulfates may also occur. Biogas purification system, based on desulfurizers with bog ore and adsorbers with activated carbon, worked with varying effectiveness, depending on the degree of bed saturation and humidity, and ambient temperature. Temporary increase of sulfur compounds in the biogas resulted in increased emissions of SO<sub>2</sub> and SO<sub>3</sub>. Periodic drop of the flue gas temperature led to the formation of sulfuric acid, which, depending on the concentration of SO<sub>3</sub> (0.1-100 ppm<sub>v</sub>), condensed at temperatures in the range of 100-150°C. Measurements of emissions and model-based calculations of the maximum immission concentrations of the analyzed pollutants (SO<sub>2</sub>,

NO<sub>x</sub>, CO, HCl, H<sub>2</sub>S) have shown that the greatest threat to the ambient air are emissions of nitrogen oxides. An interesting fact was that the share of NO<sub>2</sub> in NO<sub>x</sub>, in practice often considered at the level of 5% or ignored, was over 25%, which could be the result, as in the case of a large share of SO<sub>3</sub>, of an oxidative catalyst.

The energy biogas combustion requires its purification to a level not threatening for the apparatus and the environment. This requires reliable monitoring of the total contents of sulfur, chlorine and fluorine in the biogas. The established combustion methods of Wickbold and Lingener, which can be adapted for this purpose, have numerous disadvantages. In Wickbold's method, sample combustion takes place in a hydrogen-oxygen flame, which creates a risk of explosion at the time of initiation of the process and contributes to the high cost of the analysis. There is no possibility of adjusting and controlling the temperature in the combustion zone, which can result in incomplete oxidation. The variability of biogas composition creates additional difficulties in maintaining the correct hydrogen/oxygen/gas ratio and the stability of the combustion process. In Lingener's method combustion takes place in the presence of air, without additional fuel. Also in this case, there is no control and regulation of the combustion temperature. While analyzing biogas with this method, we shall expect lower combustion temperatures than those for natural gas, which can lead to incomplete sulfur oxidation. Bearing this in mind, I developed a method and device allowing to avoid these disadvantages and enabling simultaneous measurement of these compounds [4.2.7]. The idea behind this method is based on biogas flameless combustion and spectrophotometric or chromatographic analysis of its products. To this purpose, a prototype testing plant was built up, which, after experimental determination of the combustion process parameters, was implemented for routine tests [eg 4.2.6, 5]. Its main element is a furnace equipped with a quartz tube mounted inside a corundum tube, around which a heating element is wound. The grinding inlet of the quartz tube is connected with the burner head and the outlet is connected with the cooler. The NiCr-Ni thermocouple connected to a regulatory transformer is used to control and regulate the combustion temperature. Resistance wire is supplied via a contactor, controlled by a microprocessor-based recorder and a temperature adjuster. The recorder receives a voltage signal from a thermocouple located near the point where biogas is fed into the quartz tube. In addition, the temperature of the second thermocouple, located in front of the outlet from the furnace, is recorded on a digital millivoltmeter. The furnace is insulated with a layer of quartz wool insulation and covered with an aluminum sheet. Combustion air fed into the furnace is subject to dehumidification and preliminary purification using a column with calcium oxide, and to final purification using a column with activated carbon. Biogas is fed into the furnace with compressed nitrogen of 5.0 purity class. The mixtures of nitrogen/biogas contact with oxygen from air at the inlet head of a furnace, in temperature zone of about 1,200°C. Secure and stable combustion conditions in the quartz tube are ensured by suitably selected proportions of the air and biogas flow rates, and the relatively long contact time exceeding 7 s. As shown by the tests, the combustion of biogas in these conditions leads to full oxidation of S, Cl, and F compounds. After cooling to a temperature of 20-30°C above the dew point (approx. 60°C), combustion products are directed to a set of aspiration washers and analyzed for the content of SO<sub>2</sub>, HCl and HF. On this basis, the total content of analyzed chemical elements in the biogas is calculated. The major advantages of the method include: possibility to use one device for the simultaneous oxidation of S, Cl and F compounds, small installation cost, increased safety of handling associated with eliminating the use of hydrogen and

oxygen, selectivity. The key for the full oxidation of the analyzed compounds was experimental determination of the temperature necessary for combustion and its reliable control and automatic regulation.

Based on years of experience with biogas, given the absence of standard methodologies for the assessment of its quality, in [4.2.8] I analyzed applicable analytical methods, developed guidelines on the sampling methods and presented own proposals and recommendations for the most appropriate methodologies for biogas testing. Especially problematic is representative sampling and determination of siloxanes [4.2.10], described further.

A large set of measurement data [4.2.6, 5] was the basis of theoretical research on the intensification and modeling of the biogas treatment processes [4.2.4, 4.2.9]. Due to its availability and low costs, for the purification of biogas in Polish conditions it is common to use bog ore, a mineral comprising H<sub>2</sub>S-reactive iron compounds. Its sorption and H<sub>2</sub>S binding mechanisms are poorly understood [6-8]. There have been no sorption capacity studies performed with bog ores sorbents in real conditions. The main premise of the work [4.2.4] has been to complement the knowledge in this area. The study concerned the bog ore modified at the Institute of Chemistry and Technology of Petroleum and Coal at Wrocław University of Technology. The results have been subject to the analysis of trends, based on which I determined an average daily decrease in the efficiency of desulfurization, the average time to complete the exhaustion of the bed, the load of removed H<sub>2</sub>S during a single work cycle and the real absorptivity of the sorbent. I compared the obtained results with the results of stoichiometric calculations and laboratory tests, proving a significantly lower efficiency of the process under real conditions, which resulted from the variability of such sorbent parameters as pH, temperature, and humidity. The practical effect of research, enabling its use at similar objects, was to determine the rate of sorbent consumption and its unit cost in relation to 1,000 m<sup>3</sup> of biogas.

The continuation of studies [4.2.4] was the work of [4.2.9], which made use of a subsequent series of test results conducted at Wrocław WWTP. They were subject to a multi-parameter statistical analysis. The mathematical model of temporal variation of the H<sub>2</sub>S sorption efficiency was obtained through the analysis of three types of trends (second degree polynomial, linear and exponential), to which the corresponding regression coefficients were assigned. Their reliability was assessed with such tools of statistical analysis as dispersion diagram, correlation coefficient and relative mean deviation. On this basis, I found the exponential model to be the most reliable and I used it to determine the trend line of H<sub>2</sub>S absorption efficiency decline with sorption time, and to determine the time of bed exhaustion. The exhaustion time obtained with the model constituted approx. 75% of the time resulting from stoichiometric calculations and approx. 61% of the time obtained in the laboratory tests. On the basis of the trend lines I formulated the thesis about the influence of other factors than H<sub>2</sub>S on the decrease of sorbent activity. Among them were:

- acidification of the sorbent with CO<sub>2</sub> and organic acids generated by the decomposition of organic materials contained in the bog ore: at lower pH it changes the chemistry of H<sub>2</sub>S binding and leads to precipitation of sulfur, which blocks active pores,
- the presence of oxygen traces in the biogas, causing the oxidation of sulfides to elemental sulfur, with the above-mentioned effect,

- iron  $\text{Fe}^{+3}$  and  $\text{Fe}^{+2}$  binding with  $\text{CO}_2$ , leading to the formation of iron carbonates and bicarbonates, which blocks the bed.

I also analyzed the possibilities of intensifying the process by activation of the bog ore with chemical and physical methods to increase the specific surface area and porosity, and improve the alkali-acid, hydrophilic or hydrophobic and catalytic properties of the sorbent (calcination, loosening, alkalization, fineness).

Since 2012 I have been conducting research on a relatively new and poorly recognized subject related to the presence of siloxanes in biogas [4.2.10, 4.2.11]. My scientific interests have focused on methods of determination and removal of siloxanes from biogas and on the analysis of technological and environmental risks. Volatile methylsiloxanes, which are the products of hydrolytic depolymerisation of silicones, and their decomposition products: silanes and silanols, are among the most technologically troublesome trace compounds present in biogas. The increasing use of organosilicon compounds in various sectors of the economy, has led in recent years to a rapid increase of siloxane content in the waste and waste water, and consequently in the biogas from these sources and in the atmospheric air. During combustion, siloxanes are converted to crystalline silica, which is deposited in engines, heat exchangers and catalytic converters, blocking them with hard removable precipitates. It is now one of the major operational problems of biogas plants. To minimize them, it is necessary to reliably control the content of siloxanes in biogas. It requires the availability of proven, standardized methods of sampling and analysis. Despite numerous research in this field, such conventional methods have not been developed [9-13]. Sampling a representative probe and determination of siloxanes are difficult due to the variety of physical and chemical properties of that compounds, chemical instability, low concentrations, high volatility and unique ability to adsorb on various materials. The manner of collection seems to have a greater impact on the final result than the method of analysis. In the latter case, the most common are chromatographic methods [11,12,14-19]. However, there is no consensus about the most appropriate type of detector due to the determination of individual siloxanes [15,20,21]. In order to systematize and supplement the knowledge in this field I supervised a research project "The impact of the method and conditions of biogas sampling on the results of the chromatographic analysis of siloxanes" (2012-2013), excerpts of which I have published in the papers [4.2.10, 4.2.11]. Its essential objectives were: analysis of applicable techniques to siloxanes sampling, diagnosis of potential analytical problems, tests of the selected methodology and selection of the optimal conditions for its use. The result of the research is the choice of the absorption method in chilled methanol as the most adequate to biogas examinations, and determination of the conditions of sample aspiration. The method is suitable especially for heavier cyclic siloxanes D4, D5, D6, which are dominant in the biogas from sewage sludge. The use of insulation and adsorption methods is subject to risks of insufficient recovery of siloxanes. For this reason and due to the low selectivity as unsuitable for siloxane sampling I have considered to apply active carbon, on which certain siloxanes can polymerize. The optimizing tests of the method have been carried out under the conditions of Wrocław WWTP. Qualitative and quantitative analyses were performed using gas chromatography GC/MS. The results confirmed literature reports about the predominant share of siloxanes D4 and D5 in their total quantities [9,15,19,21-27]. However, the proportion of their participation proved to be unusual. The share of D5 was 87-92%, while according to literature data, it is usually in the range of 48-76% [19,21].

The increasing use of siloxanes results, among others, from the general conviction about their indifference to living organisms. The recently published research results indicate, however, the potential toxicity and carcinogenicity of some siloxanes, as well as the risk of their bioaccumulation [28-35]. There has been no restrictions on their use: they are not subject to restrictions on VOC, there are no indoor and outdoor air exposure limits. There are no routine controls of siloxane levels in the environment. In response to these reports, the US EPA has recently included D4 into a group of substances that require risk assessment [36]. Similar proceedings are conducted in Canada [37]. The knowledge about migration routes of siloxanes in the environment and mechanisms for their disappearance is also insufficient. These issues are addressed in the work [4.2.11]. The article analyzes new problems that have emerged in toxicology and air protection due to increasing siloxane emission and its combustion products (eg. unknown is the impact of fibrous, submicron silica, resulting from the combustion of biogas, on human health) and identifies the mechanisms of siloxane transformations in the environment. It also refers to the own research of the effectiveness of siloxane removal from biogas on a bed of activated carbon at Wroclaw WWTP, which confirmed reports in the literature [14,38] about the possibility of D4 being displaced by D5 and/or VOCs contained in the biogas. The analysis of possible transformations of siloxanes in the ambient air showed, that the main mechanism of their disappearance is the oxidation to silanols by  $\text{OH}^\bullet$  radicals. Silanols, as the compounds more soluble in water and with a lower vapor pressure, are then removed by wet deposition, and subject to slow microbiological hydrolysis. I regarded wet and dry deposition, photolysis, and oxidation with ozone and  $\text{NO}_3^\bullet$  radicals to be insignificant. In conclusion, I have presented proposals for the abatement of siloxane emission and outlined directions for further research.

## 5. Others scientific and research achievements

### 5.1. Research done before obtaining the PhD degree

From 1982 to 1984 I participated in the research on the new technology of the removal of fluorine compounds and sulfuric acid mist from the exhaust gases emitted from chemical polishing of crystals. The preliminary stage was large-laboratory scale tests of hydraulics and mass transfer kinetics of packing absorption columns, which I carried out for my Master's thesis (SPR Report No. 3/84). The results together with my economic analysis constituted one of the reasons for choosing a packing to continue the experiments in real conditions, using a prototype pilot plant at "Zawiercie" Glassworks. Field tests resulted in the development of technological project of my co-authorship (SPR report No. 6/84) and implementation of the full industry plant.

In the period of 1984-1992, the leading topic of my scientific interests was biological purification of waste gases. At that time I led the multi-scale (laboratory, pilot-plant scale and full-industrial scale) research of biological neutralization of selected air pollutants and their mixtures, including the pilot plant research in the Plywood Production Factory in Ostrow Wielkopolski. (SPR Report No. 39/85). The results were the basis for the process design of biological neutralization of formaldehyde emitted during the formation of chipboard, which I co-authored (SPR Report No. 63/85).

In the period of 1986-1990 I participated in the Central Research and Development Programme coordinated by the Centre for Research and Development of Air-Conditioning and Ventilation Industry

Equipment "BAROWENT" in Katowice entitled: "Biodegradation processes as a method of air pollutants neutralization". I developed assumptions for the construction of laboratory measurement stations to test the impingement-streaming sparger and sorption and biodegradation of pollutants (CPBR 11.2, p.1, the report SPR No. 52/87), and then I performed laboratory tests on the biological neutralization of a selected air pollutant (CPBR 11.4 p. 2, the report SPR No. 42/88). The installation constructed according to my concept, equipped with a fluidized bed column, was used to determine the hydrodynamic dependencies and studies of a mass transfer in the systems of butanol-air/water and air-butanol/active sludge suspension. Based on the results, I performed the optimization analysis, which was the basis for the selection of technological parameters of the process. Further research, which I conducted within the framework of the above-mentioned programme (CPBR 11.4 p.1, the report SPR No. 37/89), concerned the sorption of selected mixtures of air pollutants (butanol-ammonia, formaldehyde-ammonia, formaldehyde-butanol-ammonia) in the active sludge suspension. Based on its results, I suggested the optimal technological parameters of purification of waste gases emitted from the process of laminating chipboard in the conditions of Chipboard Factory in Wieruszów (ZPW). The result of the above-mentioned research are the publications [39-41], a patent [42] and my doctoral dissertation [43].

Within CPBR 11.4 (task no. 3), I conducted conceptual and design works on the technology of waste gases neutralization from the process of pressing chipboards. I was the leading author of the process design (SPR Report No. 32/87), which was the basis for the technical and construction design of the first fully industrial plant for biological purification of gases in Poland. It was built in ZPW by the consortium formed between the Environmental Protection Institute at Wrocław University of Technology and the Department of Research and Implementation of Environmental Engineering in Jelenia Góra (ZBW), coordinated by "BAROWENT" (1989-1993). As a lead designer of technological and apparatus solutions, author of the fluidized bed absorber concept and a scientific consultant from the Institute, I conducted authorial supervision over the design works and implementation research.

Overall my scientific achievements of pre-doctoral includes: presentation at the international conference, two articles, patent and 15 nonpublished research reports, including one implementation.

## 5.2. Research done after obtaining the PhD degree

After doctorate (June 1992) I continued the research on the technology of biological purification of waste gases, which ended with full-industrial implementation (December 1992). I was a consultant in elaborating the "Report on the implementation of the plant for the biodegradation of organic pollutants emitted in the process of chipboard forming in Chipboard Factory in Wieruszow" (ZBW, December 1992). I devised instruction and training materials [44,45]. An additional effect of the experience gained during the implementation research was a patent of my co-authorship [46]. I presented "The technological solutions applied in the plant for the biodegradation of air pollutants emitted from a compression process of chipboard", at the International Environmental Fair POLEKO'92, where I gave a lecture under this title [47] during the Scientific-Promotional Conference, and at the international symposium [48]. On the basis of implementation research results, I developed the guidelines for designing a series of plants [49] containing universal technical and technological indicators to design systems of capacity up to 100,000 m<sup>3</sup>/h of treated gases. Research of my co-authorship entitled "Technology of biodegradation of organic pollutants emitted in the processes of chipboard forming at the full industrial scale" was awarded the prize of the Minister of the Environment, Natural Resources and Forestry for outstanding creative achievements in the field of environmental protection, water management, geology, forestry and nature conservation (1993).

In 1993 I won a competition for the position of adjunct at the Environmental Protection Institute at Wroclaw University of Technology. Then (1995) I was appointed head of the research team involved in the waste gas purification and modeling of processes related to atmosphere protection. From that time to 2001, my research focused mainly on flue gas treatment processes. From 1995 to 1996 I headed the research project: "Simultaneous dust removal and desulfurization of combustion gases by dry sorption on the filter cake" (reports SPR No. 48/95 and 57/96). The idea behind this method is based on two mass transfer mechanisms: absorption with chemical reaction and adsorption. Desulfurization takes place mainly in the filter cake, or, more precisely, in the micro- and mesopore grains of fly ash and dosed particulate of hydrated lime in which the extraction of capillary alkali condensate and chemisorption of acidic components of flue gas are held. The main reaction product is calcium sulfate (IV) which remains in the dry state, without blocking the filter bag. For an effective, trouble-free course of these processes the cleaned flue gas must be maintained in a suitable thermodynamic state, slightly above the water dew point. The first phase of works included designing and building the model pilot plant, testing and calibrating the control and automation systems at laboratory conditions, and performing hydraulic characteristics of the plant (SPR Report No. 48/95). The principal process devices of the plant were: diaphragm-free heat exchanger type of flue gas/water (spraying column), tubular heat exchanger type of flue gas/air, sorbent dispenser and bag filter with a double-shell housing. The results of commissioning tests confirmed the assumptions and full suitability of the plant for further testing under real conditions. They were carried out during the long-term, polygon experiment using exhaust gas from the WR-10 boiler, in the Factory of Mechanized Household Equipment "POLAR" in Wroclaw. Flue gases were pre-moistened and cooled. Heat received in a diaphragm heat exchanger was used to control the temperature around the filter cake and to heat the cleaned combustion gases. The cognitive effect of experience was, among others, to determine the impact of a Ca/S ratio and a relative humidity on the flue gas desulfurization efficiency and to propose the mathematical correlation to describe that

relationship. The correlation allows to determine the economically justified dose of hydrated lime for the presumed desulfurization effectiveness, at fixed relative humidity of exhaust gases and SO<sub>2</sub> concentration. Studies have shown that to achieve above 80% of SO<sub>2</sub> removal efficiency, the relative humidity of the flue gases should be more than 70% and the Ca/S ratio greater than 1.3. To achieve a trouble-free process, the temperature around the filter cake must be maintained at least at 7°C above the dew point. The final useful effect of the research was to determine the technological balance and cost indicators and to develop guidance of control system for industrial plants. The method combines the advantages of the dry and semi-dry methods of flue gas desulfurization. SO<sub>2</sub> removal proceeds mainly in a wet phase, ensuring greater intensity, and the sorbent with the reaction products are in a dry state, so that the method is less troublesome to operate and environmentally more secure. Other advantages include: simultaneous dust removal and desulfurization, the usage of fly ash sorption properties, no sewage and waste heat recovery for conditioning of the cleaned flue gas. I presented the results of this study at the international conference [50] and published [51].

The results were so promising that they led me to attempt to develop a comprehensive flue gas treatment technology by adapting the above-described method and devices for the simultaneous removal of nitrogen oxides. On my request a research project entitled "Removal of nitrogen oxides from flue gases in filter-reactor" (SPR Report No. 48/97) was launched in 1997. The idea of the proposed method involves oxidation of NO in the gas-phase and chemisorption of the products, as in the case of desulfurization, in the filter cake. The dosed oxidant additionally enhances the removal of SO<sub>2</sub>. Simultaneously are removed other acid impurities and dust. The research was continued in "POLAR" factory, using the actual exhaust gases and the previously described pilot plant, additionally equipped with two alternative oxidant dosing systems. For testing I selected the following oxidizing agents: hydrogen peroxide, potassium permanganate, sodium hypochlorite and ozone. They were injected as a fine spray of water solutions (H<sub>2</sub>O<sub>2</sub>, NaOCl and KMnO<sub>4</sub>) to the zone of flue gas having a temperature of 150-200°C, assisting their wetting, or introduced into this zone as a gas (O<sub>3</sub>). SO<sub>2</sub> by the reaction with H<sub>2</sub>O<sub>2</sub> forms SO<sub>3</sub> and H<sub>2</sub>SO<sub>5</sub> acid which, being a strong oxidizing agent, oxidizes NO to NO<sub>2</sub>. Because the hydrogen peroxide has a higher oxidation capacity than H<sub>3</sub>O<sub>2</sub><sup>+</sup>, the process requires acidic conditions [52-54]. It is similar in the case of KMnO<sub>4</sub> (acidifying with sulfuric acid leads to the formation of anhydride manganese (VII), which is a strong oxidant [52,55]) and NaOCl, which is effective particularly in the range of pH 3-6 [56]. The most promising oxidizing agent, for the ease of its dispensing, specificity for NO and the degree of environmental hazards of the process solid products was ozone [57]. In addition to various oxidants, suitability of additives catalyzing the removal of NO<sub>x</sub>, such as NaOH and NaHCO<sub>3</sub> [58,59] was tested. The products of their reaction with SO<sub>2</sub> and SO<sub>3</sub> (e.g. Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S, NaHSO<sub>3</sub>) can promote bonding of NO<sub>2</sub> in the filter cake [60,61]. The results confirmed reports in the literature [62], provided that the effective absorption of nitrogen oxides in alkaline solution is a volume ratio of NO to NO<sub>2</sub> less than or equal to one (there is total absorption of both oxides). They also showed an evident impact of desulfurization products on the effectiveness of NO<sub>x</sub> removal. The most effective oxidizer proved to be ozone, whose utilization rate was close to the stoichiometric. The main applicative effect of the study was to propose the necessary stoichiometric excess of the investigated oxidants and hydrated lime to achieve the desired effectiveness of NO<sub>x</sub> and SO<sub>2</sub> removal, at a steady thermodynamic state of the exhaust. The proposed oxidation-sorption method of flue gas denitrification, due to moderate

investment cost, can be competitive to the known reduction methods, the more so that it intensifies desulfurization and is carried out in the same device. Moreover, it has all the previously mentioned advantages of dry and semi-dry methods, as it uses the same sorbent for both processes. The developed solutions has been patented [63-66], presented at the national and international conference [67,68] and published [69,70]. The implementation of the technology required carrying out additional research on environmental hazards of post-reaction solids. The presence of nitrates (III), sulfates (IV) and chlorides in their composition could cause problems with their safe storage and disposal. For this purpose a further research project has been launched under my direction: "Research on the quasi-dry method of simultaneous dedusting, desulfurization and denitrification of flue gases in terms of resulting post-reaction products" (SPR Report No. 33/99). The applicative result of the study was to determine the relationship between physico-chemical composition of the solid waste and its aqueous extracts and: type of oxidant, stoichiometric excess of oxidant ( $O_3$  and  $NaOCl$  were tested), the excess of  $Ca(OH)_2$ , flue gas temperature and relative humidity, and the place of dosing oxidant. On this basis, I suggested such conditions for the effective running of the process at which the resulting solid products are the least harmful to the environment [71].

The next step in the development of methods competitive for simultaneous flue gas desulfurization, denitrification and dedusting was carried out under my direction the project on "Denitrification of flue gas desulfurized by a semi-dry method, using a bag filter and a strong oxidant" (SPR report No. 35/2000). To reduce the consumption of a costly oxidant, the danger of corrosion due to the presence of  $SO_3$  in wet exhaust gases, and to minimize the risk of blocking the filter, I proposed preliminary removal of  $SO_x$  and other acidic impurities by a semi-dry method and subsequent oxidation of  $NO$  and chemisorption of  $NO_x$ , together with the residual sulfur oxides in filter-reactor [72,73]. The use of the spray absorber supplied with an aqueous suspension of hydrated lime ensured simultaneous moisturizing and cooling of the exhaust gases, and desulfurization products together with unreacted sorbent and fly ash bound  $NO_x$  in the filter cake. For  $NO$  oxidation I proposed the use of selectively acting ozone. The separation of desulfurization and denitrification processes has allowed to eliminate the main disadvantage of the established Niro-Atomizer method [74], in which both processes are carried out simultaneously, despite the different optima temperature [75]. The proposed method has allowed for the operation of the filter at a higher temperature (it was heated by the exhaust gas waste heat), which additionally ensured its greater availability. The retrofit experimental installation in the research equipment was supported with a KBN grant (Application No. IA 1970/2000, in the amount of 364,950 PLN). The results of semi-technical polygon research conducted in the "POLAR" factory confirmed the assumptions. We have achieved a high efficiency of desulfurization (>90%) and denitrification (>70%) of combustion gases at ozone consumption reduced by approx. 50% and at lower exhaust gas relative humidity than in a previously developed dry method. As a result, flue gas treatment costs have fallen almost twice. The applicative result of the study was to determine the scopes of the effective flue gas purification parameters with the proposed method (excess of sorbent and oxidant, ozone concentration, the difference between exhaust gas actual temperature and the temperature at the saturated state), which are protected by the patent [76]. The advantages of the process led in accordance with the invention are: simultaneous flue gas desulfurization, denitrification and dedusting, the ability to easily adapt semi-dry flue gas desulfurization plant, high utilization of reagents (due to separate desulfurization and

denitrification processes and recirculation of the portion of reaction products), no waste water, dry form of resulting solid waste and the lack of the need for additional activation of the sorbent by NaOH, as is in the case of the Niro-Atomizer method. The disadvantage of the method was the composition of solid products, which caused problems with their safe storage and utilization. In 2002, to solve this problem, I applied to the KBN for a research grant titled "Oxidative-sorption-reduction method of low-temperature NO<sub>x</sub> removal from flue gases". The aim of the planned study was to determine the possibility of nitrogen compounds reduction, especially nitrates (III), to N<sub>2</sub> in the filter cake, and the choice of the reducer. The application failed to obtain funding.

Parallel to the flue gas treatment I was doing research on the absorption technology of removing organochlorine impurities from waste gases (1997-1999). It was carried out under my supervision within the framework of two research projects: "Absorptive method of purifying waste gases emitted from the spray painting process" (report SPR No. 38/98), and "Intensification of absorptive removal of organochlorine impurities from waste gases" (SPR Report No. 30/99). The aim of the research, carried out with a large-scale model of experimental plant of my own design, was to develop guidelines for the new gas cleaning technology, including the selection of absorbent and optimization of operating parameters of the selected absorber type. The research was focused on real waste gases emitted from the semi-automatic line for spray painting shoes: SIREM SV3G installed in the PPH "System" in Gniezno (Poland). Physical absorption method is particularly useful for the removal of organochlorine compounds' vapors because of the possibility of solvent recovery and absorbent regeneration, and the lack of the danger of secondary air pollution of chlorine compounds, as in the methods of combustion. Its additional advantages are: no need for preheating, drying and dedusting of gases and the possibility of its use for mixtures and changeable concentrations of solvent vapors. The applied organic sorption liquids include, among others, polymers of high boiling ethers, esters, phthalates, and various oils [77-78]. However, there was no sufficient theoretical basis to design the adsorption process using them. Based on a review of the properties of potential adsorbents and preliminary results of the own study, I found silicone, paraffin and vegetable oils to be the most promising. For an absorber I chose a tubular column, with a possibility of diaphragmatic regulation and stabilization of the temperature. The essential research of the mass transfer kinetics was made in the system of air-trichlorethylene/selected oil. It used oils of different viscosities, wise- or countercurrent flow, and a column with or without packing. Based on the obtained dependencies and economic analysis I suggested the optimal working area of the absorber and developed technological design guidelines. I have presented the selected results of the research in publication [79]. Additionally, I have patented the method and system for the purification of waste gases [80].

In the period over 2002-2015, in addition to the subject of biogas presented in Section 4.3, my research interests focused on other ways of limiting the greenhouse effect, such as the use of solar energy [81,82], environmentally safe exploitation of methane clathrates [83] and natural CO<sub>2</sub> sequestration [84]. The first two works show the results of calculations of environmental profits resulting from the replacement of conventional fuels with solar collectors in a detached house and the analysis of the profitability of such an investment. The third one presents the analysis of the risks associated with the uncontrolled release of methane from clathrate deposits and environmental assessment methods of their exploitation. Article [83] identifies the interrelationships and feedbacks between the environmental

impacts of uncontrolled destabilization of clathrates. In conclusion, I proposed a technique for extracting methane from clathrates based on the exchange of CO<sub>2</sub>/CH<sub>4</sub>, which allows for the simultaneous sequestration of carbon dioxide, as a more cost-effective variant of the CCS method.

The aim of the work [84] was to propose an authoritative, in Polish conditions, model of balancing the absorption and release of CO<sub>2</sub> by forests. The analysis of literature data on a quantitative assessment of carbon dioxide sequestration has showed a significant scattering of CO<sub>2</sub> absorption indicators and a lack of universal model to forecast the net absorption of CO<sub>2</sub> by forest ecosystems under Polish conditions. The proposed methodology, based on the literature data and own calculations, is an attempt at the synthesis and verification of the current knowledge. The cognitive effect of the work are two alternative mathematical models to estimate the balance of emissions and removals of carbon dioxide by Polish forest ecosystems. The first model is based on estimating the CO<sub>2</sub> amount absorbed over the life of the trees, and the second one - on estimating biomass growth, depending on the age of the trees. The use of both models under Polish conditions gave similar results and allowed to propose a synthetic indicator of the net absorption of CO<sub>2</sub> by one hectare of a forest per year: 9 Mg/(ha·a). This corresponds to a binding of 81,800 Gg of CO<sub>2</sub> per year, which represents approx. 25% of its anthropogenic emission in Poland. I compared the obtained result with the data reported by the National Centre of Emissions Management (KOBiZE 2010), showing that the previous estimates of CO<sub>2</sub> absorption by the Polish forest ecosystems may be underestimated by approx. 35%. As this amount of CO<sub>2</sub> sequestration has a measurable financial dimension, in conclusion I suggested the inclusion of CO<sub>2</sub> absorption units to the emissions trading system. This concept was discussed as the request of the Polish government delegation at the last COP21 congress, however, there was no full consensus on this matter.

## 6. Summary of the scientific and research achievements

My academic achievements, detailed in Appendix No. 3, include: 32 articles in total (8 in the scientific journal listed in ISI Master Journal database, 6 in journals included in Journal Citation Reports (JCR) database and 14 in journals present in Polish Ministry of Science and Higher Education (MNiSW) database), 7 conference papers (including 3 on international conference), 8 patents, 5 chapters in books, 1 manual, 1 book and 116 nonpublished research. Detailed bibliometric data of my post-doctoral publications are shown in Table 1.

Table 1. Bibliometric analyze of my publications after obtaining PhD degree

No.	Journal / publication	Altogether				Scientific publications according to Art. 16, par. 2 of the Act		
		Amount of publications	$\Sigma$ IF	Points of MNiSW	$\Sigma$ Points of MNiSW	Amount of publications	$\Sigma$ IF	$\Sigma$ Points of MNiSW
1	Ecological Chemistry and Engineering	4	-	4	16	3	-	12
2	Environment Protection Engineering	5	1,448	2014-15 2011-13 2009- 9 2008- 9 2001- 6	52	3	0,796	31
3	Ecological Chemistry and Engineering S	2	0,935	15	30	2	0,935	30
4	Polish Journal of Environmental Studies	1	0,871	15	15	1	0,871	15
5	Wastewater treatment and transformation of sewage sludge - chapter	1	-	4	4	1	-	4
6	Gas, Water and Sanitary Technique	1	-	5	5	1	-	5
7	Forest Research Papers	1	-	9	9			
8	Proceedings of ECOpole	1	-	5	5			
9	Polish Solar Power Engineering	2	-	6	12			
10	Archives of Waste Management and Environmental Protection	1	-	6	6			
11	Air Protection and Waste Problems	4	-	2	8			
12	Chemical Engineering and Equipment	3	-	4	12			
13	Management of Fuels and Energy	2	-	4	8			
14	Ecology and Technique	1	-	1	1			
15	Electric Power and Economy	1	-	6	6			
16	Food Industry	1	-	2	2			
17	Patents	7	-	25	175			
18	Chapters – the rest	4	-	4	16			
19	Manuals	1	-	20	20			
20	Books	1	-	20	20			
21	Conference papers	6	-	1	6			
	$\Sigma$	50	3,254	-	428	11	2,602	97

The number of citations of my publications as of the date 30.03.2016 (without of self-citations) is:

- according to Web of Science (WoS) database: 19,
- total amount according to different search engine (eg. WoS, Scopus, Baz-Tech, Google Scholar): 48 (Appendix No. 6).

The Hirsh index according to WoS database: 3.

I am the co-author of 6 technologies, including 2 implementations.

I actively participated in 15 scientific conferences, including 6 of international scope.

I was involved in 15 research projects, including 12 in the role of manager.

I am the author or co-author of 4 mathematical models in the field of air protection engineering and based on their software.

I am the expert of the Polish National Centre for Research and Development in the field of environmental engineering, performing substantive reviews of applications for execution and funding of research projects (6 reviews in 2013-2015).

I am the author or co-author of more than 200 measuring and computational expertises in the field of impact assessments of investments on the environment.

For my most important applicative achievements I consider:

1. Development of the technology of biological gas purification, based on multi-scale research of sorption and biodegradation of selected air pollutions and their mixtures, completed of: two process designs of a prototype plant, first full industrial implementation of this type of technology in Poland, two patents, award of the Polish Minister of Environmental Protection, Natural Resources and Forestry and development of a model series of BOG plants (1984-1993).
2. Development of the quasi-dry technology of simultaneous desulfurization, denitrification and dedusting of flue gases, using a moisturizing column, a filter-reactor with an activated filter layer and strong oxidizers, on the basis of pilot scale research under real conditions, completed defining of the thermodynamic and chemical terms of effective course of processes and development of design guidelines protected by 4 patents (1995-1997).
3. Development of the semi-dry technology of simultaneous desulfurization, denitrification and dedusting of flue gases, using a spray absorber, a filter-reactor and ozone, based on the pilot scale tests in real conditions, completed determination of optimal process parameters and development of patented design guidelines (1998-2000).
4. Development and validation of a landfill biogas emission model, enabling the calculation of changes of gas productivity as a function of: weight and composition of the deposited waste, the storage period, temperature and time of degradation. The model has been repeatedly deployed to assess the impact of landfills on the atmospheric air (1998-2001). It can be used to design the degassing installation for landfills and biogas utilization plants.
5. Development of the "know-how" of the absorption method for purification of waste gases from the chlorinated hydrocarbon vapors, experimental verification of oil sorbents and apparatus for absorption, determination of the mass transfer coefficient and the optimal process conditions, completed development of the design guidelines and the patent (1997-1999).
6. Development of the way and apparatus for the simultaneous determination of total content of sulfur, chlorine and fluorine in biogas, involving the flameless biogas combustion and determination of oxidation products. The method has been implemented to examine biogas from sewage sludge (~50 SPR reports, 2002-2013).
7. Development of a regression model of temporal variation of H<sub>2</sub>S sorption efficiency on the basis of the examinations of activated bog ore sorption ability in real conditions (2003-2009). The average time of complete bed exhaustion, real sorption ability and consumption index of sorbent were determined using the model. The model can be used to design a biogas desulfurization plant and forecast the deadlines for bed exchange.

8. Research of biogas from sewage sludge at Wrocław WWTP (2002-2013), the results of which were used for the modernization and expansion of the sewage treatment plant and allowed to: determine the seasonal trends of changes of physical and chemical parameters of biogas and the relations between selected parameters, identify technological and environmental problems and determine some ways of their minimizing, develop analytical methodologies for assessing the quality of biogas, including the collection and analysis of siloxanes.

#### 7. Didactical and organizational activity

I have started my didactic job at the Wrocław University of Technology, Faculty of Environmental Engineering after obtaining the PhD degree, as a research-didactic adjunct (1993). I led, and continues to lead, lectures, seminars, laboratory and design exercises in the following subjects: Basis of environmental protection, Dispersion of air pollutants, Air protection, Waste gases purification, Abatement of air pollution emissions, Dedusting of waste gases, Emission measurement systems, and author's selectable subjects: Biogas and environment protection and Biogas – renewable energy source. I am the co-author of manual "Purification of gases. Laboratory", author of the didactic materials to design and laboratory exercises, author of the e-learning course "Energy from biogas" and author of six subject cards as the responsible person. I was the member of the Diploma Examination Commission on the uniform Master's studies, long-term student's group leader and promoter of the 55 diploma Master's and Engineer's thesis.

Positions held:

- 1995-1999 – head of the research team at Wrocław University of Technology, Environmental Protection Institute,
- 1999-2002 – head of the Laboratory of Waste Gases Purifying, Analysis and Environmental Assessment at above mentioned institute,
- 2015-until now – head of the Laboratory of Waste Gases Purifying Processes and Study of Biogas, in the structure of Department of Air Conditioning, Heating, Gas Engineering and Air Protection, Wrocław University of Science and Technology, Faculty of Environmental Engineering.

8. Awards, marks and orders

- Award of Rector of Wroclaw University of Technology for achievements in research, 1984.
- Award of Rector of Wroclaw University of Technology for achievements in the fields of technological progress and cooperation with the national economy, 1989.
- Award of Rector of Wroclaw University of Technology for professional achievements, 1991.
- Awards of Director of Environmental Protection Institute – 6 prizes for achievements in research activities in the field of technical progress.
- Award of the Minister of Environmental Protection, Natural Resources and Forestry for outstanding creative achievement in the field of environmental protection, water management, geology, forestry and nature protection for the work “Technology of biodegradation of organic pollutants emitted in the process of chipboard forming at the full industrial scale”, 1993.
- Award of the Minister of Environment in the competition “Science to protect the environment and nature” for the promoter of Master theses “Production and utilization of biogas generated by landfills in the air protection aspect”, 2000.
- Award of the Minister of Environment in the competition “Science to protect the environment and nature” for the promoter of Master theses “Assessment of the impact on atmospheric air newly created municipal landfill for the city of Wroclaw”, 2002.
- Award of the Minister of Environment in the competition “Science to protect the environment and nature” for the promoter of Master theses “Technical and economic evaluation of ecological effects of the power plant “Turow” modernization and reconstruction, in terms of air protection”, 2002.
- Award of Rector of Wroclaw University of Technology in recognition of distinctive contributions to the university, 2013.
- Gold Badge of Wroclaw University of Technology – granted by decision of the Rector, 2001.
- Bronze Cross of Merit – awarded the Polish President's decision, 2003.
- Silver Cross of Merit – awarded the Polish President's decision, 2012.

Kazimierz Gaj  
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## References

- [1] Landfill Air Emissions Estimation Model, *Office of Air Quality Planning and Standards US EPA*, 1996.
- [2] Gaj K. i in., Składowiska odpadów komunalnych jako źródła emisji zanieczyszczeń powietrza, *Chemia i Inżynieria Ekologiczna [Municipal landfills as air pollution sources, Ecological Chemistry and Engineering]*, 6(4), 1999, 337-344.
- [3] Vavilin V.A., Vasiliev V.B., Ponomarev A.V., Rytow S.V., Simulation model 'methane' as a tool for effective biogas production during anaerobic conversion of complex organic matter, *Bioresource Technology*, 48(1), 1994, 1-8.
- [4] El-Fadel M., Findikakis A.N., Leckie J.O., Numerical modelling of generation and transport of gas and heat in sanitary landfills I. Model formulation, *Waste Management and Research*, 14(5), 1996, 483-504.
- [5] Gaj K., Cybulska-Szulc H., Knop F., Parametry biogazu pochodzącego z fermentacji osadów ściekowych, *Archiwum Gospodarki Odpadami i Ochrony Środowiska, [Parameters of biogas from sewage sludge fermentation, Archives of Waste Management and Environmental Protection]*, 2, 2005, 91-98.
- [6] Rzepa G., Bajda T., Ratajczak T., Właściwości sorpcyjne rud darniowych, *Gospodarka Surowcami Mineralnymi*, 20, Z.s.2, 2004, 47-59.
- [7] Rzepa G., Ratajczak T., Skład mineralny rud darniowych a ich właściwości sorpcyjne, *Gospodarka Surowcami Mineralnymi [Sorption properties of bog iron ores, Management of Mineral Resources]*, 20, 2004, Z.s.2, 61-71.
- [8] Ratajczak T., Rzepa G., Skład mineralny polskich rud darniowych i ich właściwości sorpcyjne, *Geologia [The mineral composition of Polish bog iron ores and their sorption properties, Geology]*, 27(2-4), 2001, 458-474.
- [9] Arnold M., Reduction and monitoring of biogas trace compounds, VTT TIEDOTTEITA – Research Notes 2496, *VTT Technical Research Centre of Finland*, 2009.
- [10] Ajhar M., Wens B., Stollenwerk K.H., Spalding G., Yüce S., Melin T., Suitability of Tedlar® gas sampling bags for siloxane quantification in landfill gas, *Talanta*, 82(1), 2010, 92-98.
- [11] Raich-Montiu J., Ribas-Font C., de Arespacochaga N., Roig-Torres E., Broto-Puig F., Crest M., Bouchy L., Cortina J.L., Analytical methodology for sampling and analysing eight siloxanes and trimethylsilanol in biogas from different wastewater treatment plants in Europe, *Analytica Chimica Acta*, 812, 2014, 83-91.
- [12] Chottier C., Chatain V., Julien J., Dumont N., Lebouil D., Germain P., Volatile organic silicon compounds in biogases: development of sampling and analytical methods for total silicon quantification by ICP-OES, *Scientific World Journal*, vol. 2014, ID 537080,1-7.
- [13] Piechota G., Igliński B., Buczkowski R., An experimental approach for the development of direct-absorption sampling method for determination of trimethylsilanol and volatile methylsiloxanes by the GC-MS technique in landfill gas, *International Journal of Environmental Analytical Chemistry*, 95(9), 2015, 867-877.
- [14] Eichmann S.C., Kiefer J., Benz J., Kempf T., Leipertz A., Seeger T., Determination of gas composition in a biogas plant using a Raman-based sensor system, *Measurement Science and Technology*, 25, 2014, 1-9.
- [15] Arnold M., Kajolinna T., Development of on-line measurement techniques for siloxanes and other trace compounds in biogas, *Waste Management*, 30(6), 2010, 1011-1017.
- [16] Badjagbo K., Furtos A., Alaei M., Moore S., Sauve S., Direct analysis of volatile methylsiloxanes in gaseous matrices using atmospheric pressure chemical ionization-tandem mass spectrometry, *Analytical Chemistry*, 81(17), 2009, 7288-7293.
- [17] Badjagbo K., Heroux M., Alaei M., Moore S., Sauve S., Quantitative analysis of volatile methylsiloxanes in waste-to-energy landfill biogases using direct APCI-MS/MS, *Environmental Science and Technology*, 44(2), 2010, 600-605.
- [18] Kymäläinen M., Lähde K., Arnold M., Kurola J.M., Romantschuk M., Kautola H., Biogasification of biowaste and sewage sludge - Measurement of biogas quality, *Journal of Environmental Management*, 95(sup.), 2012, 122-127.
- [19] Rasi S., Lehtinen J., Rintala J., Determination of organic silicon compounds in biogas from wastewater treatment plants, landfills, and co-digestion plants, *Renewable Energy*, 35(12), 2010, 2666-2673.
- [20] Narros A., Del Peso M.I., Mele G., Vinot M., Fernandez E., Rodriguez M.E., Determination of siloxanes in landfill gas by adsorption on Tenax tubes and TD-GC-MS, *Proceedings Sardinia 2009, Twelfth Int. Waste Management and Landfill Symposium*, Cagliari, Italy, 2009.
- [21] Rasi S., Läntelä J., Rintala J., Trace compounds affecting biogas energy utilisation – A review, *Energy Conversion and Management*, 52(12), 2011, 3369-3375.
- [22] Liang K.Y., Li R., Sheehan J.F., Removing siloxanes: solution to combustion equipment problems, *Proceedings of the Water Environment Federation, WEFTEC*, 2002, Session 11-20, 303-313.
- [23] Tower P., New technology for removal of siloxanes in digester gas results in lower maintenance costs and air quality benefits in power generation equipment, *WEFTEC*, 2003, 78<sup>th</sup> Annual Technical Exhibition and Conference, 1-9.
- [24] Wheelless E., Gary D., Siloxanes in landfill and digester gas, *Proceedings from the Solid Waste Association of North America, 25<sup>th</sup> Annual Landfill Gas Symposium*, 2002, 29-41.
- [25] Accettola F., Haberbauer M., Control of siloxanes, in: Lens P., Westermann P., Haberbauer M., Moreno A. (eds.), *Biofuels for Fuel Cells, Renewable energy from biomass fermentation, IWA Publishing*, London, 2005, 445-454.
- [26] EPRI, Assessment of fuel gas cleanup systems for waste gas fueled power generation. *Electric Power Research Institute*, 1012763, California, 2006.

- [27] Dewil R., Appels L., Baeyens J., Energy use of biogas hampered by the presence of siloxanes, *Energy Conversion and Management* 47(13-14), 2006, 1711–1722.
- [28] Wang D.G., Norwood W., Alaei M., Byer J.D., Brimble S., Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment, *Chemosphere*, 93(5), 2013, 711-725.
- [29] Meeks R.G., Stump D.G., Siddiqui W.H., Holson J.F., Plotzke K.P., Reynolds V. L., An inhalation reproductive toxicity study of octamethylcyclotetrasiloxane (D4) in female rats using multiple and single day exposure regimens, *Reproductive Toxicology*, 23(2), 2007, 192-201.
- [30] Quinn A.L., Dalu A., Meeker L.S., Jean P.A., Meeks R.G., Crissman J.W., Gallavan Jr R.H., Plotzke K.P., Effects of octamethylcyclotetrasiloxane (D4) on the luteinizing hormone (LH) surge and levels of various reproductive hormones in female Sprague–Dawley rats, *Reproductive Toxicology*, 23(4), 2007, 532-540.
- [31] Siddiqui W.H., Stump D.G., Plotzke K.P., Holson J.F., Meeks R.G., A two-generation reproductive toxicity study of octamethylcyclotetrasiloxane (D4) in rats exposed by whole-body vapor inhalation, *Reproductive Toxicology*, 23(2), 2007, 202-215.
- [32] McKim J.M. Jr, Choudhuri S., Wilga P.C., Madan A., Burns-Naas L.A., Gallavan R.H., Mast R.W., Naas D.J., Parkinson A., Meeks R.G., Induction of hepatic xenobiotic metabolizing enzymes in female Fischer-344 rats following repeated inhalation exposure to decamethylcyclopentasiloxane (D5), *Toxicological Sciences*, 50(1), 1999, 10-19.
- [33] Burns-Naas L.A., Mast R.W., Klykken P.C., McCay J.A., White K.L., Jr., Mann P.C., Naas D.J., Toxicology and humoral immunity assessment of decamethylcyclopentasiloxane (D5) following a 1-month whole body inhalation exposure in Fischer 344 rats, *Toxicological Sciences*, 43(1), 1998, 28-38.
- [34] Burns-Naas L.A., Mast R.W., Meeks R.G., Mann P.C., Thevenaz P., Inhalation toxicology of decamethylcyclopentasiloxane (D5) following a 3-month nose-only exposure in Fischer 344 rats, *Toxicological Sciences*, 43(2), 1998, 230-240.
- [35] EPA, Siloxane D5 in Dry cleaning Application, Fact Sheet, Office of Pollution Prevention and Toxics (7404), US EPA, 2009.
- [36] Yucuis R.A., Stanier C.O, Keri C., Hornbuckle K.C., Cyclic siloxanes in air, including identification of high levels in Chicago and distinct diurnal variation, *Chemosphere*, 92(8), 2013, 905–910.
- [37] Genualdi S., Harner T., Cheng Y., MacLeod M., Hansen K.M., van Egmond R., Shoeib M., Lee S.C., Global Distribution of Linear and Cyclic Volatile Methyl Siloxanes in Air, *Environmental Science and Technology*, 45(8), 2011, 3349-3354.
- [38] Matsui T., Imamura S., Removal of siloxane from digestion gas of sewage sludge, *Bioresource Technology*, 101(1), 2010, S29-S32.
- [39] Rutkowski J.D., Czyszczon Z., Gaj K., Sravnitelnye issledovanija effektivnosti sorpcii v vode i v vodnoj vzviesi aktivnogo ilita formaldegida emitiruemogo v atmosferu v processe formirovanija drevenostruzecnych plit [Comparative study of the sorption efficiency in water and in active sewage sludge of formaldehyde emitted to the atmosphere from the process of chipboard forming]. *Zascita Atmosfery* No. 3/86 - Doklady Kollokvium po temie IV-2 SEV, Moskva 1986, wyd. VEB Kombinat Luft und Kälttechnik, Dresden, KOZ, 27-30.
- [40] Gaj K., Rutkowski J.D., Czyszczon Z., Próby zastosowania pierścieni NSW jako wypełnienia płuczki biologicznej do oczyszczania gazów odlotowych z procesu prasowania płyt wiórowych. *Ochrona Powietrza* [Attempts to apply NSW rings as biological scrubber filling, to purifying of waste gases from chipboard pressing process, *Air Protection*], 6, 1989, 157-160.
- [41] Czyszczon Z., Gaj K., Rutkowski J.D., Zastosowanie kolumny z wypełnieniem ruchomym do biologicznego oczyszczania gazów odlotowych z procesu prasowania płyt wiórowych. *Ochrona Środowiska* [Application of a column with fluidized bed to the biological treatment of waste gases from the chipboard pressing process, *Environmental Pollution Control – Journal of Polish Sanitary Engineers' Association*], 2(39), 1989, 23-26.
- [42] Rutkowski J.D., Szklarczyk M., Czyszczon Z., Gaj K., Kędziński L., Świątek J., Sposób oczyszczania gazów odlotowych z zanieczyszczeń organicznych, podatnych na biodegradację [A method of purifying exhaust gases from organic impurities susceptible of biodegradation] - patent No. PL 153092, Urząd Patentowy RP, 1991.
- [43] Gaj K., Biologiczne oczyszczanie wybranych gazów odlotowych w modelowej instalacji doświadczalnej z ruchomym wypełnieniem – praca doktorska [Biological treatment of selected waste gases using model experimental plant with fluidized bed – doctoral dissertation]. *Raporty Inst. Inż. Ochr. Środ. PWroc.* 1992, Ser. PRE nr 13/92.
- [44] Gaj K., Materiały do szkolenia obsługi prototypowej instalacji do biologicznego oczyszczania gazów w ZPW Wieruszów [Training materials on handling of the prototype installation for a biological waste gases purification in ZPW Wieruszów], ZBW, październik 1992.
- [45] Gaj K., Gnach T., Kobec E., Technologiczna instrukcja obsługi prototypowej instalacji do biologicznego oczyszczania gazów w ZPW Wieruszów [Technological user manual of the prototype installation for a biological purification of waste gases in ZPW Wieruszów], ZBW, listopad 1992.
- [46] Bryl J., Gaj K., Kaczmarski K., Sposób oczyszczania półek/rusztów aparatów kolumnowych i urządzenie do oczyszczania półek/rusztów aparatów kolumnowych [A method and device for cleaning shelves/grids of columns] - patent No. PL 169233 B1, Urząd Patentowy RP, 1996.
- [47] Rutkowski J.D., Gaj K., Rozwiązania technologiczne, zastosowane w instalacji do biodegradacji zanieczyszczeń powietrza, emitowanych z procesu prasowania płyt wiórowych. Konferencja Naukowo Techniczno-Promocyjna na Międzynarodowych Targach Ekologicznych POLEKO'92 [The technological solutions applied in the plant for the biodegradation of air pollutants emitted from a compression process

- of chipboard. Conference on Science and Technology Promotion at the International Environmental Fair POLEKO'92] Poznań, Poland, 1992.
- [48] Gaj K., Rutkowski J.D., Bryl J., On the application of trickling filter bed reactors to the treatment of odoriferous flue gases: a case study. International Symposium BIO'94 *Biotechnology in Environmental Protection*, Świnoujście, Poland, 1994.
- [49] Gaj K., Rutkowski J.D., Opracowanie wytycznych projektowych typoszeregu instalacji do biologicznego oczyszczania gazów, z węzłem absorpcji w postaci kolumny z ruchomym wypełnieniem [Developing of the type series design guidelines of installations for biological gas purification, with absorption device in the form of a column with a fluidized bed], ZBW, 1993.
- [50] Gaj K., Knop F., Badania efektywności odsiarczania spalin metodą quasi suchej sorpcji w placku filtracyjnym - skala pilotowa [Examinations of flue gas desulfurization efficiency using quasi dry sorption in a filter layer - pilot scale]. 5-th International Symposium *Integrated air quality control for industrial and commercial sectors*, Międzyzdroje, Poland, 1997.
- [51] Gaj K., Knop F., Intensyfikacja odsiarczania spalin w warstwie filtracyjnej filtra workowego. *Ekologia i Technika* [Intensification of flue-gas desulphurization in the filter layer of bag filter, Ecology and Technique], 2(26), 1997, 19-22.
- [52] Littlejohn D., Chang S.G., Removal of NO<sub>x</sub> and SO<sub>2</sub> from flue gas by peracid solutions. *Ind. Eng. Chem. Res.*, 29, 1990, 1420-1424.
- [53] Cooper H.B.H., Removal and recovery of nitrogen oxides and sulfur dioxide from gaseous mixtures containing them, U.S. Patent 4,426,364, 1984.
- [54] Thomas D., Vanderschuren J., The absorption-oxidation of NO<sub>x</sub> with hydrogen peroxide for the treatment of tail gases. *Chem. Eng. Sc.*, 51(11), 1996, 2649-2654.
- [55] Lambert D., McGowan T.F., NO<sub>x</sub> control techniques for the CPI. *Chem. Eng.*, 6, 1996, 98-101.
- [56] Yang C.L., Shaw H., Perlmutter H.D., Absorption of NO promoted by strong oxidizing agents: 1. Inorganic oxychlorites in nitric acid. *Chem. Eng. Comm.*, 143, 1996, 23-38.
- [57] Pollo I., Jaroszyńska-Wolińska J., Sposób usuwania tlenków azotu z gazów odlotowych [A method of removing nitrogen oxides from exhaust gases]. Patent PL No. 115926, 1982.
- [58] Chu P., Rochelle G.T., Removal of SO<sub>2</sub> and NO<sub>x</sub> from stack gas by reaction with calcium hydroxide solids, *JAPCA*, 39, 1989, 175-179.
- [59] Donnelly J.R., Felsvang K. S., Morsing P., Veltman P.L., Process for removal of nitrogen oxides and sulfur oxides from waste gases. European Patent Application No. 0077170, 1983.
- [60] Kobayashi H., Takezawa N., Niki T., Removal of nitrogen oxides with aqueous Solutions of Inorganic and organic Reagents. *Environ. Sci. & Technol.*, 11(2), 1977, 190-192.
- [61] Gross M., SHL Verfahren zur SO<sub>2</sub>/NO<sub>x</sub>-Simultanreinigung von Gasen. *Vortrag im Haus der Technik*. Essen 1985.
- [62] Kuroпка J., Absorpcja alkaliczna tlenków azotu. *Ochrona Środowiska* [Alkaline absorption of nitrogen oxides, *Environmental Pollution Control – Journal of Polish Sanitary Engineers' Association*], 2-3(46-47), 1992, 45-48.
- [63] Gaj K., Knop F., Suchy sposób oczyszczania spalin [A dry method of flue-gas purifying] - patent No. PL 188482 B1, Urząd Patentowy RP, 2005.
- [64] Gaj K., Knop F., Mech J., Suchy sposób oczyszczania spalin [A dry method of flue-gas purifying] - patent No. PL 188483 B1, Urząd Patentowy RP, 2005
- [65] Gaj K., Knop F., Suchy sposób oczyszczania spalin [A dry method of flue-gas purifying] - patent No. PL 188485 B1, Urząd Patentowy RP, 2005.
- [66] Gaj K., Knop F., Cybulska H., Suchy sposób oczyszczania spalin [A dry method of flue-gas purifying] - patent No. PL 192995 B1, Urząd Patentowy RP, 2006.
- [67] Gaj K., Knop F., Nowa sucha metoda jednoczesnego odpylania, odsiarczania i odazotowania spalin. IV Sympozjum POL-EMIS'98 „Ograniczenie Emisji Zanieczyszczeń do Atmosfery”, Szklarska Poręba. [A new dry method of simultaneous dedusting, desulphurization and denitrification of flue gases. 4 Symposium „Abatement of emissions to the atmosphere”], Szklarska Poręba, Poland, 1998.
- [68] Gaj K., Knop F., Semi-dry flue gas cleaning method using a strong oxidizing agent and an activated filter cake. 17-th *International Symposium on Combustion Processes*, Poznan, Poland, 2001.
- [69] Gaj K., Knop F., Oczyszczanie spalin przy wykorzystaniu silnego utleniacza i aktywnej warstwy filtracyjnej. Część I [Flue gas purification using a strong oxidizing agent and active filter layer. Part I]. *Inżynieria i Aparatura Chemiczna*, 37(6), 1998, 16-18.
- [70] Gaj K., Knop F., Oczyszczanie spalin przy wykorzystaniu silnego utleniacza i aktywnej warstwy filtracyjnej. Część II [Flue gas purification using a strong oxidizing agent and active filter layer. Part II]. *Inżynieria i Aparatura Chemiczna*, 38(1), 1999, 22-24.
- [71] Gaj K., Trzepierczyńska I., Knop F., Cybulska H., Stałe produkty poreakcyjne suchej metody równoczesnego odpylania, odsiarczania i odazotowania spalin przy wykorzystaniu ozonu i aktywnej warstwy filtracyjnej [Solid post-reaction products of dry method of simultaneous dedusting, desulfurization and denitrification of flue gases, using ozone and active filter layer]. *Inżynieria i Aparatura Chemiczna*, 39(4-5), 2000, 5-10.
- [72] Gaj K., Koncepcja adaptacji półsuchej metody odsiarczania spalin do równoczesnego procesu ich odazotowania. IV Sympozjum POL-EMIS'98 „Ograniczenie Emisji Zanieczyszczeń do Atmosfery” [A concept of adaptation of semi-dry flue gases desulfurization method for the simultaneous process of denitrification, 4 Symposium POL-EMIS'98 „Abatement of emissions to the atmosphere”], Szklarska Poręba, Poland, 1998.

- [73] Gaj K., Możliwości adaptacji absorpcyjnych metod odsiarczania spalin do ich równoczesnego odazotowania przez zastosowanie silnego utleniacza. *Gospodarka Paliwami i Energią [Adaptation possibilities of absorption methods for flue-gas desulfurization to their simultaneous denitrification using strong oxidant, Management of Fuels and Energy]*, 47(4), 1999, 16-19.
- [74] Donnelly J.R., Felsvang K.S., Morsing P., Veltman P.L., Process for removal of nitrogen oxides and sulfur oxides from waste gases, European Patent No. EP0077170 B1, 1986.
- [75] Chu P., Rochelle G.T., Removal of SO<sub>2</sub> and NO<sub>x</sub> from stack gas by reaction with calcium hydroxide solids, *JAPCA*, 39(2), 1989, 175-179.
- [76] Gaj K., Półsuchy sposób oczyszczania spalin [*A semi-dry method of flue-gas purifying*] - patent No. PL 188484 B1, Urząd Patentowy RP, 2005.
- [77] Kuhn in the forefront of VOC removal technology, *Filtration & Separation*, 33(4), 1996, 266,
- [78] Heck G., Müller G., Ulrich M., Reinigung lösungsmittelhaltiger Abluft – alternative Möglichkeiten, *Chem. Ing. Tech.*, 60(4), 1988, 286-297.
- [79] Gaj K., Mech J., Robaszkiewicz J., Investigation of selected oils as absorbents of the chlorinated hydrocarbons. *Environ. Prot. Eng.*, 27(2), 2001, 71-79.
- [80] Gaj K., Robaszkiewicz J., Bryl J., Sposób i układ do oczyszczania gazów odlotowych z chlorowcopochodnych węglowodorów [*A method and system for purification exhaust gases from chlorinated hydrocarbons*] - patent No. PL 195706 B1, Urząd Patentowy RP, 2007.
- [81] Gaj K., Pakuluk A., Efekty ekologiczne zastosowania kolektorów słonecznych w domu jednorodzinnym, *Polska Energetyka Słoneczna [Ecological effects of the use of solar collectors in a detached house, Polish Solar Power Engineering]*, No. 2-4/2010, 1/2011, 49-53.
- [82] Gaj K., Pakuluk A., Efekty ekonomiczne zastosowania kolektorów słonecznych w domu jednorodzinnym, *Polska Energetyka Słoneczna [Economic effects of the use of solar collectors in a detached house, Polish Solar Power Engineering]*, No. 2-4/2010, 1/2011, 43-48.
- [83] Cieślak S., Gaj K., Hazards of uncontrolled methane release from clathrates analyse and environmental evaluation of extraction methods, *Environ. Prot. Eng.*, 40(3), 2014, 99-111.
- [84] Gaj K., Pochłanianie CO<sub>2</sub> przez polskie ekosystemy leśne, *Leśne Prace Badawcze [Carbon dioxide sequestration by Polish forest ecosystems, Forest Research Papers]*, 73(1), 2012, 17-21.