AUTHOR'S SUMMARY OF PROFESSIONAL ACCOMPLISHMENTS

(English version)

dr. Mariusz Grabda

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1. Personal data:

First and last name: **Mariusz Grabda**

2. Academic diplomas and titles

Diplomas and Titles:

1994 **Higher Education Graduation Diploma** (with the highest final grade) and receiving the M.Sc. degree issued by the Hugo Kołłątaj Academy of Agriculture, Faculty of Horticulture in Cracow

Title of thesis: „The use of cocoa husk in the cultivation of geranium cv. Ringo White"

The supervisor of the thesis was Doc. dr inż. Włodzimierz Sady.

2000 **Doctoral Diploma in Technical Sciences, Specialization of Environmental Engineering** issued by Institute of Environmental Engineering of the Polish Academy of Sciences in Zabrze

Title of thesis: „The dynamics of the transformations of physicochemical and biological properties of the soils in the Podhale region heated by geothermal water energy"

The supervisor of the thesis was Prof. dr hab. inż. Czesława Rosik-Dulewska. The reviewers of the thesis were Prof. dr hab. inż. Jan Siuta and Prof. dr hab. Eugeniusz Kołota.

Other certificates:

1994 **Certificate of completion of 2-years Pedagogical Preparation Course** (with the highest final grade) organized by the AGH University of Science and Technology in Cracow

1997 **Certificate of completion of 2-semesters Postgraduate Studies** (with the highest final grade) in the field of Protection of Natural Environment and Mineral Resources issued by the AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection in Cracow

Title of thesis: "Methods for sewage sludge disposal. Solutions for the natural utilization of sewage sludge from municipal wastewater treatment plant in Opole"

3. Details of research career

11.1994-12.1995 senior technical assistant

Faculty of Horticulture, the Hugo Kołłątaj Academy of Agriculture in Cracow

10.1996-present assistant (10.1996-07.2000), assistant professor (08.2000–7.2009), assistant (08.2009-present)

(since 02.2002 on the leave due to research internship in foreign research centers)

Institute of Environmental Engineering of the Polish Academy of Sciences in Zabrze

11.2012-03.2017	senior assistant professor/lecturer **Institute of Multidisciplinary Research for Advanced Materials Tohoku University in Sendai (Japan)**
04.2018-10.2018	*associate professor* **Waseda University, Faculty of Science and Engineering in Tokyo (Japan)**
02.2019-obecnie	*assistant professor, leader/manager of research project* **Geeral Tadeusz Kosciuszko Military Academy of Land Forces in Woclaw, Faculty of Security Sciences, Institute of Safety Engineering**

Scientific trainings:

02.2002-10.2002	NATO Advanced Fellowship Programme Scholarship **Icelandic Horticultural College w Hveragerdi (Iceland)**
04.2003-03.2005	postdoctoral fellowship **Institute of Multidisciplinary Research for Advanced Materials Tohoku University in Sendai (Japan)**
04.2006-10.2011	research associate **Institute of Multidisciplinary Research for Advanced Materials Tohoku University in Sendai (Japan)**
11.2012-03.2017	senior assistant professor/lecturer **Institute of Multidisciplinary Research for Advanced Materials Tohoku University in Sendai (Japan)**
04.2018-03.2019	visiting researcher **Kagoshima University, Faculty of Science in Kagoshima (Japan)**
04.2018-10.2018	associate professor **Waseda University, Faculty of Science and Engineering in Tokyo (Japan)**

My research interests concentrate on widely defined area of waste management. In particular, they relate to recycling and recovery of valuable fractions (organic, mineral, metallic, energy, etc.) present in the waste, using processes/technologies of possible smallest effect to the natural environment.

Prior to earning a doctoral degree (2000), my research interests focused on recycling of organic waste:

- use of cocoa husks - waste from the food industry, as a substitute for peat in the cultivation of geranium cv. Ringo White (M. Sc. project);
- natural disposal of sewage sludge for soil fertilization and improvement (postgraduate project)
- evaluation of technical and economic feasibility for development of regional sewage sludge management plan in the Silesian province (project conducted at IEE PAS in Zabrze).

As well as on recovery and utilization of "waste heat":

- "cascade" recovery of heat of geothermal water for intensive crop production at Podhale region (doctoral thesis);
- application of low-temperature geothermal heat in order to extend the growing season of grassy turf of sport fields (postdoctoral project conducted at Hveragerdi in Iceland, in the framework of the NATO Advanced Fellowship Programme).

During a postdoctoral fellowship at Tohoku University (Japan), I joined an innovative research on recovery of valuable metal fractions from waste. This experience has expanded my research interests to recycling of industrial wastes. Some achievements obtained during that study are basis of my recent habilitation.

In Japan, I participated in many interdisciplinary projects related to waste. For example, I predicted physical-chemical and thermodynamic properties of selected toxic organic compounds formed during thermal treatment of waste, as well as I tried to predict their formation and environmental fate. The following research projects were related to this subjet:

- predictions of thermodynamic properties of selected Brominated Flame Retardants (BFRs) with a usage of Density Functional Theory (DFT)
- predictions of the solubility of selected Persistent Organic Pollutants (POPs) using quantum-mechanical calculation methods (Gaussian, COSMO-RS)
- measurements of thermodynamic properties of selected polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and Brominated Fame Retardants using Differential Scanning Calorimetry (DSC).

4. Scientific achievement

4.A. Title

Separation of metals from industrial wastes by bromination-evaporation and with a usage of ionic-liquids, for the purpose of environmental protection and sustainable development

4.B. Series of scientific publications and patent – consisting the scientific achievement

Publications

After each publication the following information are provided in brackets: (impact factor of the journal at the year of publishing, number of points according to list of the Ministry of Science and Higher Education at the year of publishing, number of all citations/excluding self-citation according to Web of Science (WoS) and Scopus (as for February 10th, 2019).

1. [A1] **Grabda M.**, Oleszek-Kudlak S., Shibata E., Nakamura T. „Gas phase thermodynamic properties of PBDEs, PBBs, PBPs, HBCD and TBBPA predicted using DFT method", (Elsevier) *Journal of Molecular Structure: Theochem,* 2007, 822, 38-44 (IF 1.112, MNiSW 15, WoS 12/12, Scopus 11/11)
2. [A2] **Grabda M.**, Oleszek-Kudlak S., Rzyman M., Shibata E., Nakamura T. „Studies on bromination and evaporation of zinc oxide during thermal treatment with TBBPA", (American Chemical Society – ACS) *Environmental Science & Technology*, 2009, 43, 1205–1210 (IF 4.63, MNiSW 24, WoS 23/13, Scopus 25/13)
3. [A3] **Grabda M.**, Oleszek-Kudlak S., Shibata E., Nakamura T. „Influence of temperature and heating time on bromination of zinc oxide during thermal treatment with tetrabromobisphenol A", (American Chemical Society – ACS) *Environmental Science & Technology*, 2009, 43, 8936–8941 (IF 4.63, MNiSW 24, WoS 13/5, Scopus 16/6)
4. [A4] **Grabda M.**, Oleszek-Kudlak S., Shibata E., Nakamura T. „Vaporization of zinc during the thermal treatment of ZnO with tetrabromobisphenol A (TBBPA)", (Elsevier) *Journal of Hazardous Materials*, 2011, 187, 473-479 (IF 4.173, MNiSW 45, WoS 17/12, Scopus 19/14)

5. [A5] Oleszek-Kudlak S., **Grabda M.**, Shibata E., Nakamura T. „Alternative method for pyrometallurgical recycling of EAF dust using plastic waste containing Tetrabromobisphenol A", (De Gruyter) *High Temperature Materials and Processes*, 2011, 30, 359-366 (IF 0.242, MNiSW 15, WoS 4/4, Scopus 5/5)
6. [A6] **Grabda M.**, Oleszek S., Shibata E., Nakamura T. „Study on simultaneous recycling of EAF dust and plastic waste containing TBBPA", (Elsevier) *Journal of Hazardous Materials,* 2014, 278, 25-33 (IF 4.529, MNiSW 45, WoS 13/12, Scopus 16/15)
7. [A7] **Grabda M.**, Oleszek S., Shibata E., Nakamura T. "Distribution of bromine and metals during co-combustion of polycarbonate (BrPC) and high-impact polystyrene (BrHIPS) wastes containing brominated flame retardants (BFRs) with metallurgical dust", (Springer) *Journal of Material Cycles and Waste Management,* 2018, 20(1), 201-203 *(accepted on November 2016),* (IF 1.693, MNiSW 20, WoS 1/1, Scopus 1/1)
8. [A8] **Grabda M.**, Panigrahi M., Oleszek S., Kozak D., Eckert F., Shibata E., Nakamura T. „COSMO-RS screening for efficient ionic liquid extraction solvents for $NdCl_3$ and $DyCl_3$", (Elsevier) *Fluid Phase Equilibria*, 2014, 383, 134-143 (IF 2.2, MNiSW 30, WoS 9/5, Scopus 10/6)
9. [A9] **Grabda M.**, Oleszek S., Panigrahi M., Kozak D., Eckert F., Shibata E., Nakamura T. „Theoretical selection of most effective ionic liquids for liquid-liquid extraction of NdF_3, (Elsevier) *Computational and Theoretical Chemistry*, 2015, 1061, 72-79 (IF 1.403, MNiSW 20, WoS 2/2, Scopus 2/2)

Patent

10. [A10] Oleszek S., **Grabda M.**, Shibata E., Nakamura T. „Method of separation of metals present in electric arc furnace dust", patent P.406547, received by Polish Patent Office on December 16th, 2013

Summary of scientific indicators of the Achievement:

IF: 24.612	MNiSW: 238	WoS: 96/66	Scopus: 105/73

The results of research works constituting the achievement were published in 9 scientific articles listed in the database of Journal Citation Reports (cumulative impact factor: 24.612; the number of MNiSW points: 238), and were used to propose a technological process protected by patent.
The subject of the scientific achievement was actively popularized at 55 international conferences and seminars, among them as much as 21 oral presentations (5 invited) and 10 poster presentations were presented by habilitant.
In 2011, the research regarding separation of metals by bromination-evaporation process, were awarded by HONDA Awards for Development in Recycling Technologies Award from the Clean Japan Center.
Whereas, the innovative use of COSMO-RS in order to study the extraction properties of ionic liquids for recycling of rare earths aroused great interest among scientific community (12 conference presentations, including 3 invited lectures).

4.C. Description of purpose of the study, obtained results and scientific importance of the work

Introduction

The motivation and scientific objective of my study was to develop a new methods for the recovery of metals from industrial waste.
The results of the study presented in publications A1-A7 were used to propose an innovative method for separation of metals present in the electric arc furnace dust (EAFD) by bromination-evaporation. In 2011, these works were awarded Honda Award for Development in Recycling Technology given by the Clean Japan Center. Since December of 2013, the proposed process is protected by patent [A10].

The results presented in publications A8-A9 concern the method for selection of ionic liquids suitable for recycling of rare earth metals from waste, which was developed by me. To my knowledge, this is the only, ever published in the scientific press, comprehensive tool for selection of ionic liquids extractants *a priori* (without the need for costly and time-consuming experimental research). Experimental studies confirmed the excellent effectiveness of ILs preselected by the theoretical method. The achieved results are therefore an important step towards the development of a novel process for recycling rare earths with a use of ionic liquids.

Steel production in an electric arc furnace (EAF) generates a flue by-product called EAF dust (EAFD). EAFDs are classified as hazardous wastes and pose a serious problem for environmentally acceptable disposal [1]. Because of environmental restrictions, the cost of disposing of these residues is high [2]. For example, disposal of EAFD in the United States costs 200 million US dollars per year [3]. On the other hand, EAFDs are rich in valuable metallic oxides and can be used as secondary raw materials in the production of zinc [1–14], iron, and lead [3].

The average concentration of iron in the dust is approximately 30 mass%, which is present mostly as magnetite (Fe_3O_4) and frankonite ($ZnFe_2O_4$) [15]. The largest non-ferrous portion of EAFD is zinc (present as zincite, ZnO, as well as in frankonite), and its concentration varies between 7% and 40% (depending on the ratio of galvanized scrap used) [3]. The concentration of lead does not exceed a few percent of the total mass of EAFD. Taking into account the above concentrations, the worldwide generation of EAFD (Table 1) represents a possible recovery of about 1.14 million tons of zinc [1,2], approximately 285 thousand tons of lead, and huge amount of iron-oxide-rich residues, which can be used as valuable recovered resources in steel production [9]. The development of an effective and efficient separation processes for the heavy metals is therefore an urgent matter.
In Poland, according to the Ministry of the Environment [16] operates 7 steel plants equipped with electric arc furnaces, which in 2003 produced approx. 3 million tons of steel, generating 545 thousand tons of dust EAFD.

Although numerous zinc recovery processes have been developed, only pyrometallurgical recovery has achieved commercial success [1], and this is mainly limited to variations of the Waelz rotary-kiln process [1,17] (Tab. 1). Unfortunately, their main disadvantage is their high energy consumption and cost; the Waelz rotary kiln process requires temperatures of 1200–1300 °C [2,10].

Table 1. Generation and recycling of the dust from electric arc furnace, in thousand tons/year [17]

	NAFTA1)	SEAISI2)	China	EU 273)	Other	WORLD
Generation of EAFD	760 ,1	1157,0	724,2	1024,4	2129,3	5795,0
Recycling of EAFD by process of:	810,0	427,0	0	1071,0	250,0	2558,0
- Waelz	735,0	270,0	0	831,0	210,0	2046,0
- RHF	25,0	62,0	0	40,0	20,0	147,0
- other	50,0	95,0	0	200,0	20,0	365,0
Zinc recovery	186,0	98,0	0	246,0	58,0	588,0

1) member countries of North American Free Trade Agreement; 2) member countries of South-East Asian Iron and Steel Institute, 3) 27 member countries of European Union

In the last decade, an alternative method based on selective chlorination and evaporation of zinc using waste poly(vinyl chloride) (PVC) as a chlorination agent was proposed [1,6–11]. Unfortunately, the initial study of the chlorination–evaporation process in a laboratory-scale furnace [10] indicated that the process may be associated with undesired volatilization of about 17% of the iron in the form of $FeCl_3$ [10]. Additionally, in order to obtain a high rate of zinc separation, a temperature of about 1000

°C is required to complete the zinc volatilization [10]. This means that the energy consumption of the chlorination–evaporation method is probably only slightly lower than that of the costly Waelz process.

In Poland, only a small portion of EAFD is recycled. Most is used by cement plants as a feedstock for clinker production, or is stored, whereby the latter solution has harmful effects on the environment and is associated with high fees. [16] Therefore, further investigations for alternative methods of recycling of metals present in EAFD are needed.

An alternative method of pyrometallurgical recycling of EAFD using waste plastics containing Brominated Flame Retardants (BFRs) was investigated in my studies (Fig. 1).

Currently, most of the world production of bromine (approx. 38%) is used for production of BFRs. Among them, the most widely used is tetrabromobisphenol A (TBBPA), especially for electronic and electric devices (E & E). It is estimated that more than 75% of the E&E produced in the world today comprises the compound [18].
Less commonly used BFR is hexabromocyclododecane (HBCD), and, until recent restrictions, also polybrominated diphenyl ethers (PBDE), polybrominated biphenyls (PBB) and polybrominated phenols (PBP). Although the manufacture of some of the compounds were recently stopped, these substances are still present in stream of waste plastics requiring disposal.

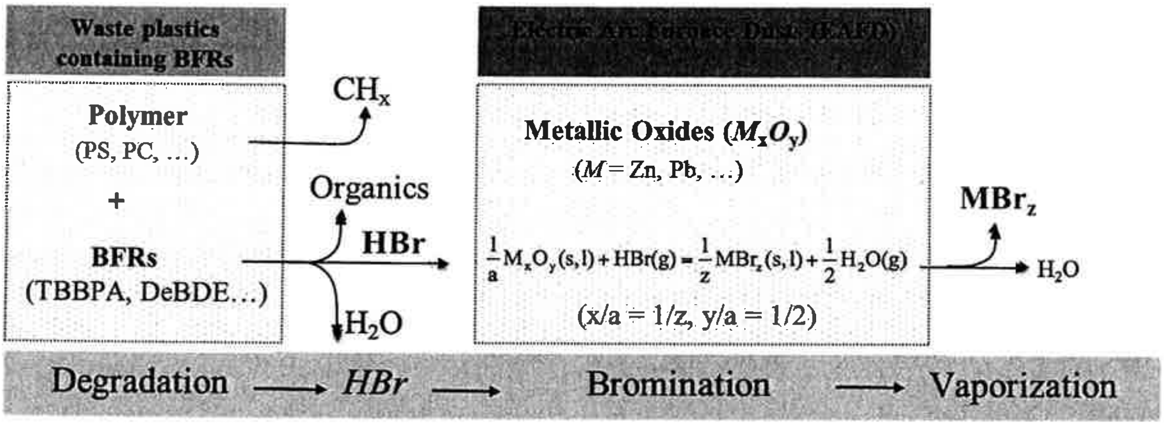

Figure 1. Schematic of separation of metals present in electric arc furnace dust (EAFD) during co-combustion with waste plastic containing brominated flame retardants (BFRs).

The amount of produced E&E is increasing steadily year after year, thus increasing the amount of waste of electronic and electrical equipment (WEEE) demanding for safe disposal. It is estimated that, nearly 8 million tonnes of such waste is generated each year in the EU alone, and the annual growth is estimated at 3-5%. Approx. 20-50 million of such waste is generated worldwide every year [18].
About 90% of the produced TBBPA is used in the production of epoxy, phenolic and polycarbonate resins, applicable in the finishing of printed circuit boards (PCB) of electronic appliances. The remaining 10% TBBPA is mainly used in the copolymers, acrylonitrile-butadiene-styrene (ABS) and high impact polystyrene (HIPS). Common practice of the industry to strengthen the effect of flame retardancy is to add antimony trioxide (Sb_2O_3) to the resin (synergistic effect).

The increasing amount of the emerging products containing TBBPA, and the fact of short life-spam of these products, raises the need for a reasonable way of disposal of the waste containing BFRs. Thermal treatment of plastic waste (incineration, co-incineration, pyrolysis) is a very common practice, as it allows to recover organic fraction of the waste (recovery of energy from carbon-rich plastics using a waste-to-energy technologies (WtE) as well as inorganic fractions (recovery of metals from printed circuit boards).
During the thermal treatment, TBBPA present in the waste plastics, decomposes rapidly and produces large quantities of inorganic bromine gas, mainly in the form of a very reactive hydrogen bromide (HBr) and Br_2 [19-23].

My study focused on identification of possibilities to use the inorganic bromine for separation of metals present in the EAFD.

In case of rare earth elements (REEs), their industrial importance is constantly growing due to their growing use in many high-tech devices [24].
For example, Dy and Nd are widely used in plasma display panels [25], inorganic electroluminescent materials [26], mobile phones, disc drivers and, above all, in permanent magnet [27] of hybrid cars and wind turbines.
REEs rarely exist in the earth's crust in concentrated, and thus suitable for economically viable exploitation, mineral deposits. Starting from the 90s, a major producer of these metals is China. Recently, however, the country decided to limit the supply of REEs on the world markets due to the growing internal high-tech industry. It is, therefore, extremely important to recycle these scarce metals from used products.
Spent permanent magnets from the automobile industry have been highlighted as valuable secondary resources of REE. They may contain more than 20 wt% Nd and 4–5 wt% Dy [28-29].

However, despite many efforts [28-32] on the development of methods of recycling of these metals, still a small number of them is recovered (no more than 10% REE in 2011) [33]. One of the most important reasons for this, are technological problems and the high costs of the proposed solutions. In the case of REE recycling from used magnets, extraction by hydrometallurgical, pyrometallurgical and gas methods as well as by hydrogen decrepitation were proposed. Each of these methods, however, has many disadvantages which limit the possibility of their widespread use. In the case of pyrometallurgy, the main problem is a huge energy demand as well as a large amount of new solid waste generated. In the case of hydrometallurgical methods, the problem is related to high complexity (multi-stage) of the recovery process, and consequently, a huge amounts of toxic solvents requiring subsequent disposal.

Therefore, there is a growing interest in application of ionic liquids (ILs) for recycling of these metals [34-38], as an environmentally friendly alternative to conventional solvent extraction.
This is mainly due to unique physicochemical properties of ionic liquids, such as: low melting point [39-41], a negligible vapor pressure [42], low flammability [43], high thermal stability [44], a large electrochemical window [45]. For these reasons, they are often called "green" solvents for the technologies of the future.

ILs are organic salts being liquids at room temperature. They consist entirely of weakly coordinating ions (organic cation, and organic or inorganic anion). Tuneability of ILs is one of their major advantages. By chemical modification of the ions, or by selecting a proper ions combination, an IL with the properties desired for a given application can be obtained [46-47].
Presently, more than 1,000 different ILs are commercially available. However, there is the possibility to design completely new compounds, even on the basis of already available ions. Physical and chemical properties of ionic liquids, link between their properties and combinations or molecular modification of their ions, and particularly their usefulness for certain processes (eg. for metals extraction and separation) is still poorly understood!
However, synthesis of new liquids, and experimental tests of their suitability for a particular process, would be extremely cost intensive and time consuming.
Because the experimental realization of such studies would be significantly time consuming and cost intensive, a judicious prescreening of the various combinations of ions in terms of their suitability for recycling of metals *a priori* is required.
The common structure-interpolating group contribution methods (GCMs), such as UNIFAC, are not applicable for IL systems because of lack of many experimental parameters. A sufficient database of such experimental values for IL systems is not yet available.

The purpose of my work was to study possibility of application of ILs for recycling of REEs. In particular, I have been interested in selecting ILs suitable for extraction for the metal ions of Neodymium [Nd^{3+}] and Dysprosium [Dy^{3+}] from aqueous solutions of their chloric and fluoric salts, which are formed during technological leaching of the metals from waste.

In order to select the optimal ionic liquids for extraction of the REEs of my interest, I proposed to use an innovative *conductor-like screening model for realistic solvents* (COSMO-RS) [48].

References (cited in the above introduction)

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Objective and scope

The general objectives of my study in the field of separation of the metals present in the EAFD were:
a) to clarify whether the gaseous inorganic bromine (HBr, Br_2) released during thermal degradation of waste plastics containing TBBPA can be used for separation and evaporation of zinc present in the EAFD,
b) to clarify mechanism of the bromination reaction of zinc oxides present in EAFD by gaseous products of thermal degradation of TBBPA and other BFRs present in waste plastics, and
c) to identify and optimize the factors affecting the separation efficiency of zinc during co-incineration of both groups of waste.

Because of the complex chemical composition of two groups of waste many reactions and processes occurring during their thermal treatment were overlapping The situation made achievement of the objectives of (b) and (c) difficult. Therefore, I decided to start the investigation from reactions occurring during heating of mixtures of pure compounds (TBBPA + zinc oxides), followed by more complex chemical compositions (TBBPA + EAFD) → (resins containing BFRs + EAFD).

The detailed scope of the research included:

1. Computational works [A1]
    1. creation a coherent database of thermodynamic properties of the main BFRs present in plastic waste as well as all congeners resulting from their gradual degradation, and on that base, to perform molecular consideration of stability, degradation and transformation of these compounds,
2. Experimental works [A2-A7]
    - 2.1. investigation of thermal degradation of TBBPA,
    - 2.2. investigation of behavior of zinc oxide (ZnO) during thermal treatment with TBBPA,
    - 2.3. recognition of mechanism of bromination reaction between ZnO and HBr generated during thermal degradation of TBBPA, as well as identification and optimization of factors effecting efficiency of the reaction,
    - 2.4. investigation of behavior of zinc bromide ($ZnBr_2$) generated in the above reaction, and optimization of factors affecting efficiency of its vaporization from solid residue,
    - 2.5. investigation of behavior of main metals' oxides present in EAFD, i.e. ZnO, ZnF_2O_4, PbO, Fe_2O_3 during co-combustion of EAFD with TBBPA and TBBPADGA (tetrabromobisphenol A diglicydyl ether – main component of epoxy resins),
    - 2.6. investigation and optimization of condition for co-combustion of EAFD with waste epoxy, polycarbonate and polystyrene resins containing commercial mixture of BFRs, for maximal separation of Zn and Pb from Fe-rich solid residue,
    - 2.7. proposal of novel method for recovery of metals from EAFD by their co-combustion with plastic wastes containing BFRs [A10].

In the study regarding an application of ionic liquids for recycling of rare earth metals, detailed scope of my works included:

4. Computational works [A8-A9]
    4.1. creation of molecular database of 138 ions of ionic liquids (88 cations and 50 anions) (works carried out with usage of quantum-mechanical calculations and software of: COSMO*build*, Turbomole, COSMO*conf*),
    4.2. prediction of selected physical-chemical properties (viscosity, octanol/water partition coefficients) of 138 ions and 4,400 ionic liquids resulting from combination of the ions, and investigation the relationship between the properties and molecular structure of the compounds (works performed with usage of Turbomole, COSMO*conf*, COSMO*therm*),
    4.3. selection of 900 ionic liquids characterized by highest hydrophobic properties, and prediction of chemical potentials of Nd and Dy in the selected ionic liquids,
    4.4. selection of 4 ionic liquids of "first choice" and 7 ionic liquids of "second choice" suitable for extraction of ions of Nd and Dy from aqueous solutions of their salts,
5. Experimental works
    5.1. proposal of the selected ionic liquids for experimental tests, proposing of experimental conditions for the study, and substantive support for the experimental works.

Obtained results

Referring to the mentioned motivation and scientific objectives of the study, main results obtained in my works are presented below.

The first area of research was:

Separation of metals present in electric arc furnace dusts by bromination-evaporation method

Thermodynamic properties of BFRs

My first achievement was development of a coherent theoretical database of thermodynamic properties of all congeners of main BFRs, ie. polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), polybrominated phenols (PBPs), hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBPA).

Although the production and use of some of them were suspended, the substances are still present in the stream of waste plastics waiting for disposal. As a result of improper storage or uncontrolled burning, BFRs present in such wastes can contaminate the environment by various toxic congeners formed as a result of their gradual degradation/de-bromination and/or transformation. Thermodynamic properties of these substances are very little known, and a scarce available data refer only to major congeners.

I performed quantum-mechanical predictions of heat capacity, entropy, enthalpy, Gibbs free energy of 439 congeners of brominated flame retardants (209 congeners PBDE, 209 congeners PBB, 19 congeners PBP and HBCD and TBBPA) using density functional theory (DFT) and the program of Gaussian03. The obtained database was published in the form of a 15-page annex to the publication of [A1]. This is the first ever published in the scientific literature, so complete list of thermodynamic properties of all congeners of brominated flame retardants.

The coherent and homogeneous database allowed me to carry out many thermodynamic considerations and to draw important conclusions, for example: (1) to identify the most and the least thermodynamically stable congeners of PBDE, PBB, PBP, (2) to estimate relationship between the thermodynamic properties of these compounds and the number/location of bromine in their molecular structure, (3) to conduct thermodynamic interpretation of degradation path of PBDE and (4) their transition to polybrominated dibenzofurans (PBDFs). I have shown, among others, the "thermodynamic preference" for transformation of PBDEs to these toxic compounds, and noticed that the preference intensifies along with the progress of de-bromination of PBDEs.

Behavior of pure metal oxides during co-incineration with TBBPA:

Zinc oxide (ZnO):

Preliminary studies [A2] on utilization of inorganic bromine evolving during thermal decomposition of TBBPA for bromination-evaporation of zinc oxide (ZnO) were carried out in inert atmosphere (Argon), under dynamic heating of mixtures of these substances with differential scanning calorimetry (DSC) (1 °C / min), and in a laboratory-scale furnace (10 °C / min) (Fig. 2).

Initial mixture of ZnO TBBPA was prepared in a stoichiometric mass ratio of 3.34:1 w/w, i.e. at which amount of bromine present in the TBBPA is enough for complete bromination of ZnO according to the reaction: TBBPA + ZnO → BA + $ZnBr_2$). Several additional experiments were carried out with an increased amount of TBBPA in the mixture of 5.17: 1 w/w.

I have shown that the decomposition of TBBPA occurs immediately after melting of the substance (ie. at 180 °C), and intensifies at temperature of 260 °C (studies with DSC) or 290-340 °C (studies with furnace). I estimated that, in the applied experimental conditions, as much as 53-62% of bromine contained in TBBPA is released in the inorganic form, mainly as HBr, which then reacts with ZnO contained in the heated mixture. Detailed analysis of the solid residue and the vaporized phases revealed that the bromination occur at 272 °C (DSC), or in a temperature range of 290-340 °C (laboratory furnace), with the reaction efficiency of 41% and 64%, respectively.

I have found that further heating of the mixture of these substances did not significantly increase the amount of brominated zinc, while the increase of TBBPA in a heated mixture (5.17: 1 w/w) increases the efficiency of the bromination reaction to 81%.

The initial evaporation of formed $ZnBr_2$ was observed at 340 °C, while a clear intensification of the process was observed not before 550 °C. At 650 °C, approx. 45% of the formed bromide evaporated from the solid residue. I recognized that the low evaporation bromide can be limited by insufficient temperature used in the experiments and may be restrained by formation of char, which results from cross-linking of high-molecular products of degradation of TBBPA.

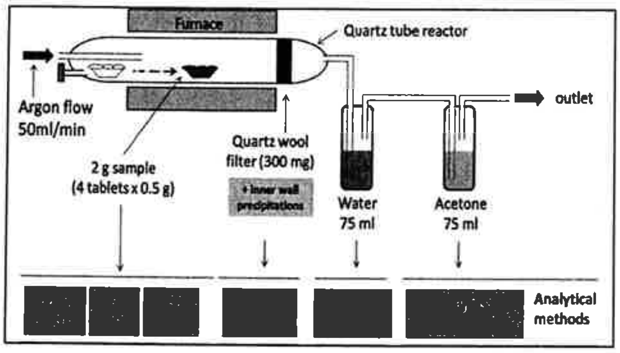


Figure 2. Schematic of experimental procedures for furnace (dynamic heating 10 °C / min) and overview of analytical methods

Effect of temperature and time on bromination of zinc: The influence of temperature and time on bromination of zinc oxide during heating with TBBPA was studied and described in details in paper [A3]. In the study, I focused on changes taking place during isothermal heating (10-140 min) of TBBPA:ZnO (3.34: 1 w / w) at 11 different temperatures ranging from 230 to 420 °C.

Effect of temperature: Moment of initial de-bromination of TBBPA, and initial formation of zinc bromides, were precisely determined by application of comprehensive analytical procedure (gas chromatography coupled with mass spectrometry, GC-MS, and X-ray diffraction, XRD), electron probe microanalysis (EPMA), inductively coupled plasma mass spectrometry (ICP-MS) which allowed to investigate decomposition products present in all phases (solid, condensed and gaseous). The procedure allowed to precisely state that the initial de-bromination of TBBPA (5%) begins at temperature of 240 °C, and that all inorganic bromine released at this temperature immediately and almost entirely (99%) reacts with the ZnO. The maximum amount of inorganic bromine (63%) is released from TBBPA as soon as at 280 °C. At this temperature, the highest level of bromination ZnO (69%) was observed. Further increase in temperature does not cause any significant changes in availability of inorganic bromine or efficiency of bromination reaction. This is due to the fact that at 280 °C, TBBPA which is the original source of bromine, is already completely decomposed to more simple bromo-organic forms (as indicated by GC-MS of solid residue). Isothermal heating was found to decrease temperature of initial decomposition of TBBPA as well as temperature of maximum bromination of zinc by 50-60 °C, in comparison to studies conducted using dynamic heating (10 °C/ min).

Effect of time: The effect of time on the efficiency of the bromination of ZnO was investigated by heating the mixture of TBBPA:ZnO (3.34:1 w/w) until complete decomposition of all bromo-organic compounds in the solid residue (heating time ranged from 10 to 140 minutes depending upon the temperature) at four selected temperatures (250, 270, 290 and 310 °C). A very strong impact of heating time on efficiency of bromination ZnO was observed. The impact was largest at lower temperatures, weakened along with their growth, and almost disappeared at 310 °C. At this temperature, the maximum efficiency of the bromination reaction has been achieved within the first 10 min of heating. It was found that this dependence is a direct result of progressive decomposition of TBBPA, ie. a process in which inorganic bromine, capable to react with ZnO, is gradually liberated. The efficiency of bromination of zinc oxide increased steadily until complete degradation of the original (TBBPA) and secondary (bromo-organic products of TBBPA decomposition) sources of reactive Br in the solid residue. The studies have shown, that under the applied conditions, a maximum of 65% of the bromine contained in the BFR was released in inorganic form (the other portion evaporated from solid residue in the form of bromo-organic compounds re-condensing in the cooler part of the reactor and on the filter), and its dominating majority (approximately 96%) reacted with zinc oxide.

A small portion of unreacted inorganic bromine (a maximum of 8%) evaporated from the sample, presumably due to prior evaporation from the top layer of the heated mixture, or as a results of subsequent secondary de-bromination of condensed products.

Additionally, effect of weak oxidizing conditions (Ar + 5% Oxygen) on the process of bromination ZnO during thermal treatment with TBBPA was investigated. The conditions were chosen on the base of information obtained from DOWA company (Japanese company involved in the development of recycling technologies) pointing out that similar conditions occur inside rotary kiln during combustion of plastic wastes.

Treatment at such conditions revealed, however, no effect on the de-bromination of TBBPA and bromination of ZnO. The lack of any significant effect is probably due to the fact that the bromination reaction takes place in a molten dense phase of TBBPA, which effectively isolate particles of ZnO from outside oxidizing conditions. Lack of any ZnOBr compounds in the solid residue (investigated by XRD and EPMA) seems to confirm the presumption.

In next paper [A4] I presented my studies on evaporation of zinc bromide from the residue. For the purpose of these investigations, the experimental works were carried out at higher temperature (490-950 °C) in inert (Ar), weak (Ar + 5% oxygen) and strongly oxidizing (Ar + 20% oxygen) conditions. The studies have shown strong dependence of evaporation of $ZnBr_2$ from temperature, time, and from concentration of oxygen in the experimental atmosphere.

Application of higher temperatures for heating the samples resulted in faster evaporation of the zinc bromide. I noticed that evaporation of 98% of $ZnBr_2$ from the residue heated at 550 °C requires as much as 80 minutes of heating. While, similar evaporation (97%) can be achieved after just 10 min of heating at temperature higher of 100 °C. I found that complete (100%) evaporation of $ZnBr_2$ requires temperature of 950 °C (heating for 40 min).

I noticed, however, that application of so high temperatures led to carbothermic reduction of unreacted ZnO present in the solid residue by carbon-rich char. The process begins at 850 °C, and the resulting zinc gradually evaporates from the residue in metallic form (2% of metallic zinc evaporated at 850 °C, 11% at 900 °C and 18% at 950 °C).

The study revealed very strong correlation between the amount of char and evaporation of $ZnBr_2$. I found that char can have an inhibitory effect on the evaporation of the metal bromide. The inhibitory effect decreases, however, with the progress in char degradation, and eventually disappears when the amount of char falls below 15%. I have shown that the key to eliminate the slowing effect of char is to accelerate its degradation by application of atmosphere enriched in oxygen (Ar + 20% oxygen). Such conditions reduced temperature of complete (98-100%) evaporation of $ZnBr_2$ to 550 °C, without significant impact on the bromination of ZnO. The above discovery decided that further research (using actual EAF dust and brominated resin) were performed mainly at the selected experimental conditions, ie. isothermal heating for 80 min at 550 °C under oxidizing atmosphere containing 20% of oxygen.

Progress in studies on bromination and evaporation of ZnO during heating with TBBPA conducted so far were collectively summarized in [A5].

Franconite ($ZnFe_2O_4$)
Zinc is present in EAFD in the form of zincite, ZnO, and zinc ferrite, $ZnFe_2O_4$. In studies [A6] carried out with TBBPA:$ZnFe_2O_4$ (3:1 w/w) under oxidizing conditions at 550 °C, I found that as much as 70% zinc initially present in $ZnFe_2O_4$ was separated as $ZnBr_2$ from the non-brominated iron. For comparison, at inert conditions, the bromine released from degrading TBBPA reacted with both zinc and iron present in ferrite (49% and 6%, respectively).

Behavior of metals present in EAFD during co-incineration with TBBPA and real resins containing BFRs:

The same experimental conditions were used for co-incineration of TBBPA with real EAFD (3:1 w/w) [A6]. In The studies, high bromination of zinc and lead (80 and 88%, respectively) was achieved, while evaporation of formed bromides from solid residue amounted to 86% and 21%, respectively. None of iron oxide was brominated at oxidizing condition of the tests.
Under inert condition (carried out for comparison), efficiency of bromination of zinc and lead rose to 93 and 71%, respectively. It led, however, to an undesirable bromination of iron (2%), and significant "losses" of inorganic bromine (24%) which did not react with any metals present at EAFD.

Therefore, the isothermal heating of the mixture for 80 minutes at 550 °C under oxidizing atmosphere (Ar + 20% vol. O_2) were selected as the most promising conditions for separation of zinc and lead from a real EAFD during co-combustion with real resins containing BFRs.

In further studies, carried out under the above conditions, were applied tetrabromobisphenol A diglycidyl ether (TBBPADGE) (which is the main component of the epoxy resins) [A6], and two resins commonly used in electrical, electronic and construction materials, ie. BrPC: polycarbonate resin containing TBBPA [A7], and BrHIPS: high-impact polystyrene resin containing commercial mixture of BFRs and Sb_2O_3 [A7].

In case of TBBPADGE with EAFD (3:1, w/w), separations of zinc and lead from iron-rich residue were even greater than in case of pure TBBPA, and amounted to 85 and 81% at oxidizing, and 84 and 33% at inert conditions, respectively. In neither case bromination of iron was observed.
In case of thermal treatment of EAFD with the BFRs-containing resins, majority of inorganic bromine released from BrPC was gaseous HBr and partially Br_2, while in the case of BrHIPS-containing Sb_2O_3 - $SbBr_3$.

The studies have shown that all of the forms of bromine reacted with zinc and lead oxides, but not with iron, present in the dust (Fig. 3). Their conversions to bromides were, however, higher in the case of co-combustion with BrPC than BrHIPS.
I analyzed impact of mass ratio of Resin/EAFD, and effect of particle size on efficiency of bromination of metals.
It was stated that the greatest bromination of zinc and lead occur in samples mixed at ratio of 6:1 and 9:1 w/w. At these samples, as much as 78% of ZnO and 97% PbO were transferred to bromides in case of BrPC, and 47% and 70% in case of BrHIPS (Fig. 3).

It was stated that the further grinding of plastics does not increase the availability of bromine for the bromination reaction. It was shown that heating of the resins leads to formation of char (more abundant during combustion of BrHIPS than BrPC), which then undergoes slow gradual oxidation under aerobic conditions. In the inert conditions, however, the abundant char resists evaporation of the resulting bromides, and participate in carbothermic reduction of PbO.

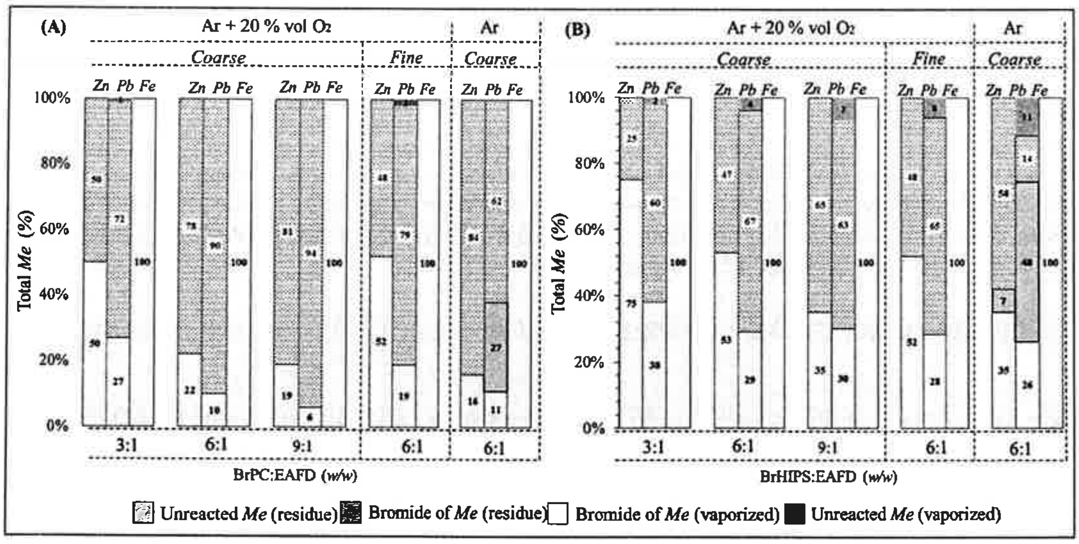


Figure 3. Distribution of zinc (Zn), lead (Pb), and iron (Fe) during isothermal heating of (A) BrPC:EAFD; and (B) BrHIPS:EAFD at 550 °C for 80 min under varied experimental conditions (varied ratios of the mixture components, varied particle size of plastics, inert and oxidizing conditions).

Reactions of bromination of metals present in EAFD are closely linked to physical-chemical changes occurring in the thermally treated resins.
In order to identify the changes, I heated the mixtures of BrPC and BrHIPS with EAFD (6:1 w/w) at eight different temperatures, ie. 190, 230, 290, 340, 420, 490 and 550 °C. The resulting solid residues were then analyzed by scanning electron microscopy (SEM) (Fig. 4). The procedure allowed for identification and characterization of transitions occurring in the heated resins (Fig. 5).

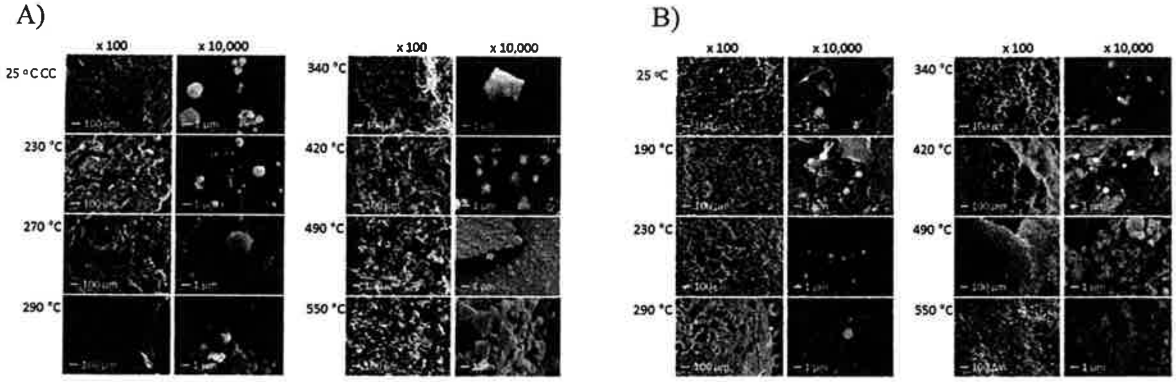
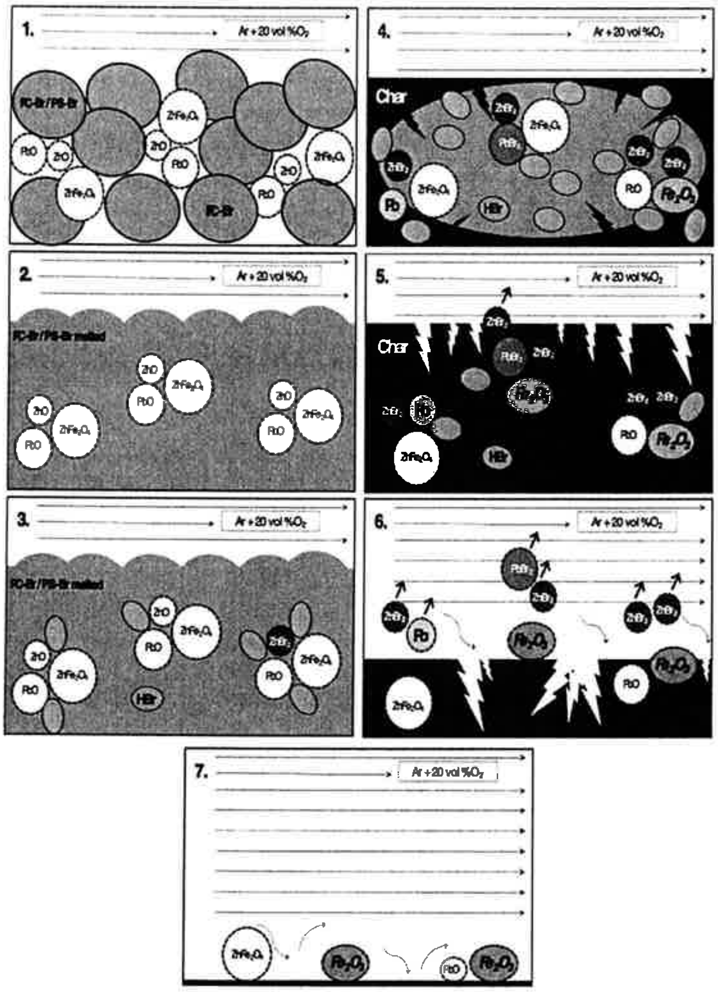


Figure 4. SEM photos of solid residues obtained after isothermal treatment of: A) BrPC with EAFD (6:1 w/w) and B) BrHIPS with EAFD (6:1 w/w) at selected temperatures under oxidizing conditions (Ar 20 vol% O_2).

The key stages of the changes have been described in the patent [A10]), and included:

1. Melting of the resins
Melting of the resin is the first and essential step of the process. Initial melting of BrPC in the mixture with EAFD is clearly visible in SEM image of the solid residue obtained at 230 °C (Fig. 4A). Advanced melting can be seen on a SEM image taken at 270 °C.
In case of BrHIPS, tablets containing its mixture with EAFD lengthened and swelled at temperature range of 190-290 °C. Zoomed SEM image of solid residue obtained at 190 °C (Fig. 4B) showed an initial melting of the polymer, while at 230 °C particles of EAFD dissolved in molten polymer matrix are clearly visible (Fig. 4B).

The molten resins form a dense phase which tightly covers the particles of EAFD, and thus isolates the metal oxides from external conditions. This mechanism is shown schematically in Fig. 5-2.



1. Compressed mixture of BFRs-based resin with EAFD;
2. Melting of the resin;
3. Evolution of HBr from gradually decomposing resin, and initial bromination of ZnO present in the dust;
4. Intense decomposition of BFRs present in the resin, bromination of ZnO and PbO present in the dust, formation of char, and carbothermic reduction of some lead oxide to metallic lead;
5. Initial oxidation of the char and vaporization of volatile $ZnBr_2$;
6. Progressive oxidation of char and volatilization of formed bromides and metallic lead from the residue;
7. Complete oxidation of char and remains of unreacted and non-vaporized $ZnFe_2O_4$ and PbO.

Figure 5. Concept of successive changes taking place during thermal treatment of BFRs-contained resins (BrPC, BrHIPS) with EAFD under oxidizing conditions.

2. Decomposition and de-bromination of the resins / bromination of metals

Melting of the resin is followed by thermal degradation of the polymer. At this stage, an intensive release of inorganic bromine is taking place. Particles of metals oxides (lead and zinc) present in EAFD are immersed in the molten resin and carefully separated from outer oxidizing (or inert) atmosphere (Fig. 5-3). Because of vapor pressure of the released Br is very high, the bromination of the metal oxides (Equation 1) is immediate:

$$\frac{1}{a}M_xO_y(s,l) + HBr(g) \rightarrow \frac{1}{z}MBr_z(s,l) + \frac{1}{2}H_2O(g) \tag{1}$$

where, M = Pb, Zn or Fe; $x/a=1/z$; $y/a=1/2$.

The formed bromides evaporate gradually (Fig. 5-5) from the solid residue, according the Equation 2:

$$MBr_z(s,l) \rightarrow MBr_z(g) \tag{2}$$

3. Charring

Simultaneously to decomposition of the resin proceeds linking of degradation products of high molecular weights. This leads to the formation of the carbon-rich residue called char (Fig. 5-4, 5-5, 5-6). The char consists of closed pores: SEM photo of the solid residue taken at 340 °C (Fig. 4) shows cheese-like structure of the char. This specific feature of the char constitutes an excellent matrix for the carbothermic reduction of metallic oxides, as the process may proceed inside the char even under oxidative conditions.

The metallic oxides are embedded in the matrix being effectively isolated from exterior (oxidizing) atmosphere. Therefore, they undergo gradual reduction to metallic forms according to Equation 3:

$$M_xO_y(s,l) + yC(s) \rightarrow xM(s,l) + yCO(g) \tag{3}$$

It should be noted, however, that at the applied experimental conditions only partial carbothermic reduction of lead oxide, but none of zinc, was detected.

4. Oxidation of char / complete evaporation of metallic bromides

The oxidizing conditions accelerate decomposition of the char by its oxidation to carbon oxides according to equations 4 and 5:

$$C(s) + O_2(g) \rightarrow CO_2(g) \tag{4}$$

$$C(s) + 1/2O_2(g) \rightarrow CO(g) \tag{5}$$

Along with the progress in char degradation, its closed pores gradually open. The process allows for gradual liberation of all volatile compounds trapped before in the char. The mechanism of this process is shown schematically in Fig. 5-5,6,7. The disappearance of the pores in char can be seen on the SEM images of solid residues taken in the 420 °C (Fig. 4A) and 490 °C (Fig. 4B).

Under inert conditions, however, instead of fast oxidation, the char proceeds slow thermal decomposition.

In summary, it must be emphasized that melting of the resin facilitates contact between inorganic bromine and metals present in EAFD, while oxidation of char facilitates evaporation of formed bromides at low temperature.

Another area of my research was:

The separation of ions of rare earth metals from aqueous solutions of their salts with ionic liquids

My research in the area began from construction of molecular database of ions of ionic liquids, and chloride and fluoride salts of Neodymium and Dysprosium. Molecular structures of all compounds were constructed with usage of COSMO*build* program. The quantum-mechanical optimization of the chemical structures, and COSMO calculations of the above molecules were done with BP (Becke-Perdew) DFT and def-TZVP (triple-ζ polarized valence) in the TURBOMOLE program. Then, the conformational analysis of the molecules was performed using COSMO*conf* software, and the most stable conformers, ie. characterized by the lowest electron energies were identified.

Using the above procedure, I created a molecular database containing 88 cations of ionic liquids, belonging to different chemical groups, and 50 different anions of ionic liquids [A8], as well as chloride [A8] and fluoride [A9] salts of Nd and Dy.

With the use of COSMO*therm* program, I estimated the octanol/water partition coefficients of all isolated ions (138 ions), and the partition coefficients of the ionic liquids resulting from the ions combination (4400 ionic liquids). Then, I analyzed dependency of this property from the molecular structure of the ions [A8].

I have shown, for example, that most cations are characterized by high affinity for organic phase ($\log_{10}K_{OW} > 4$) (Fig. 6). I found that extremely strong hydrophobic properties are manifested by ions containing long alkyl chains. In contrast to cations, anions of the ionic liquids, with the exception of a few containing fluorinated alkyl chains, manifest affinity for water ($\log_{10}K_{OW} < 0$) (Fig. 6) [A8].

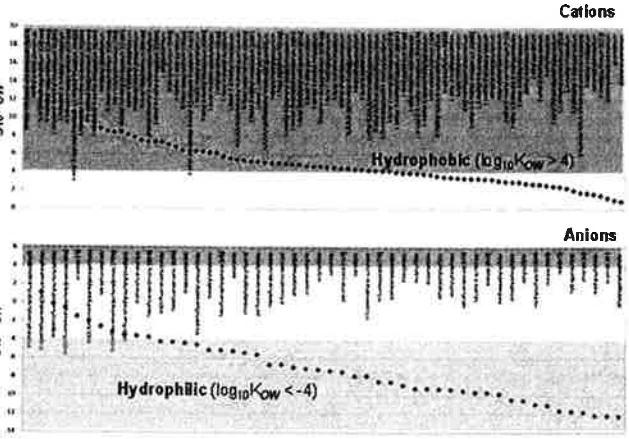


Figure 6. Estimated octanol/water partition coefficients of 88 isolated cations (top) and 50 isolated anions (bottom) of ionic liquids used in the study.

It was shown that the ionic liquids derived from combinations of these ions exhibit, in most cases, hydrophilic properties ($\log_{10}K_{OW} < -4$) (Fig. 7). The hydrophilicity of ionic liquids is highly unfavorable for the process of liquid-liquid extraction, as may lead to undesired mixing of the ionic liquid with feed solution. Therefore, I identified and selected 900 hydrophobic ionic liquids, resulting from combination of 30 cations and 30 anions characterized by highest K_{OW} (Fig. 7) [A8-A9].

Moreover, I estimated viscosities of the 900 selected ionic liquids [A8]. The works were conducted in the COSMO*therm* software, using a quantitative structure-activity relationship (QSAR) and descriptors proposed by Eiden et al. (J. Phys. Chem. B, 2011, 115, 300-309).

Selection of ionic liquids manifesting extractive properties for ions of Nd and Dy were performed by calculating chemical potentials of the metal salts in 900 selected ionic liquids. The estimates were done using the program of COSMO*therm*. The computations were performed on several different systems, involving various models of the salts dissociation and solvation: A) Me^{3+}; B) $Me(H_2O)_{7\text{-}8}^{3+}$, and C) $MeCl(H_2O)_{7\text{-}8}^{2+}$ reported in the scientific literature (Ciupka et al., 2010, *Phys. Chem. Chem. Phys.*, 12, 13215-13223; Steele & Wertz., 1997, *Inorg. Chem.* 16, 1225-1228).

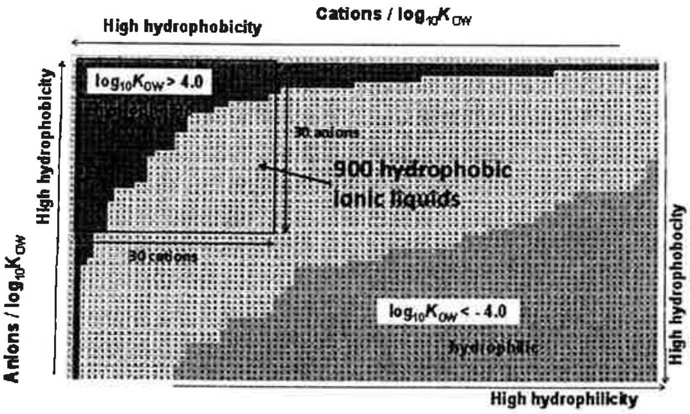


Figure 7. Estimated octanol/water partition coefficients of 4400 ionic liquids (numerical values are invisible), including highlighted 900 most hydrophobic liquids.

The obtained results (Fig. 8) allowed me to identify group of ions exhibiting an extremely strong chemical affinity (drastic drop in chemical potentials) with respect to both metals. Among them are: cation of: dodecyldimethyl(3-sulfopropyl)ammonium [DDSP]$^+$, and anions of: bis(2,4,4-trimethylpentyl)phosphinate [TMPP]$^-$, decanoate [DeA]$^-$ and benzoate [BA]$^-$ (Tab. 2) [A8]. These ions were classified be me as "first choice".

I suggested that effective IL extractants for Nd and Dy should include any of the above ions. Selection of a proper counter-ions were based on the previously estimated properties, and aimed to obtain the IL characterized by low viscosity and negligible miscibility with the aqueous phase (Table. 3).

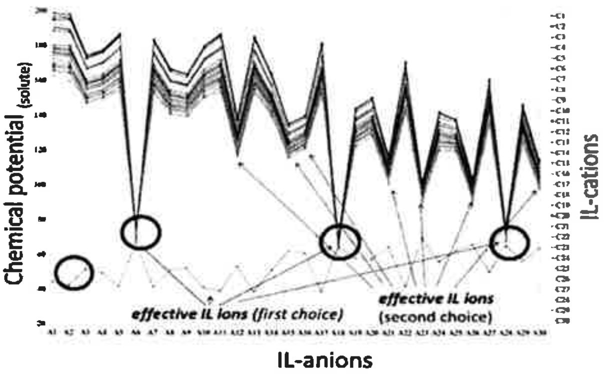


Figure 8. Averaged chemical potentials of Nd (Nd^{3+}, $Nd(H_2O)_8{}^{3+}$, $NdCl(H_2O)_7{}^{2+}$) and Dy (Dy^{3+}, $Dy(H_2O)_{7\text{-}8}{}^{3+}$, $DyCl(H_2O)_{7\text{-}8}{}^{2+}$) estimated in selected ionic liquids.

Table 2. Molecular structures of the ions of the "first choice" as well as the counter-ion of [T66614]$^+$ and [TPTP]$^-$ selected for liquid-liquid extraction of Nd and Dy with the use of COSMO-RS.

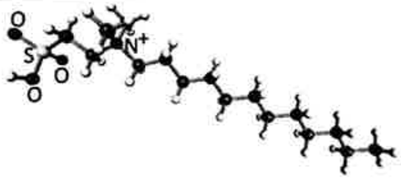
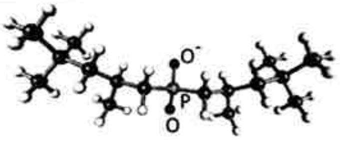
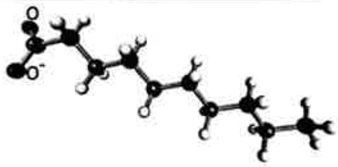
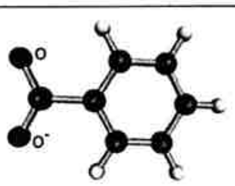
Ions of "first choice"	Molecular structure
dodecyldimethyl(3-sulfopropyl)ammonium [DDSPA]$^+$	
bis(2,4,4-trimethylpentyl)phosphinate [TMPP]$^-$	
decanoate [DeA]$^-$	
benzoate [BA]$^-$	

Table 2. Continued

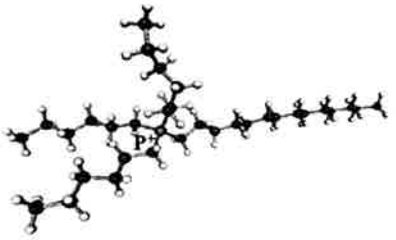
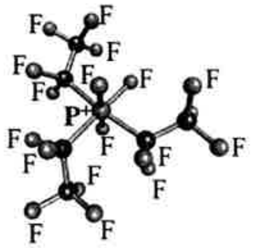
Counter-ions	
trihexyl(tetradecyl)phosphonium $[T_{66614}]^+$	
tris(pentafluoroethyl)trifluorophosphate $[TPTP]^-$	

Table 3. Ionic liquids containing the ions of the "first choice" for the liquid-liquid extraction of Nd and Dy selected by COSMO-RS.

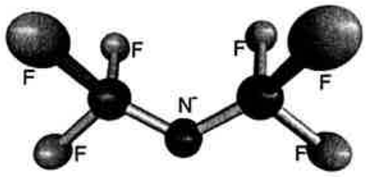
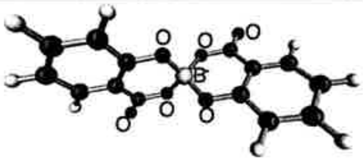
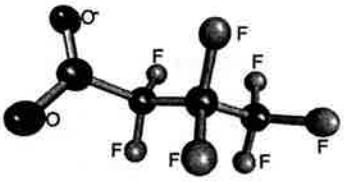
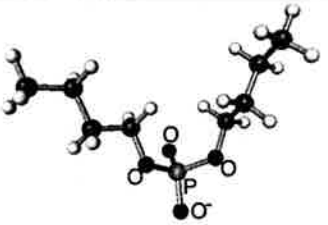
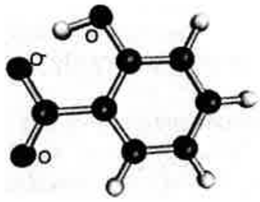
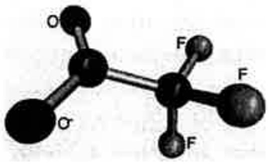
Ionic liquid		$\mathbf{log_{10}}\boldsymbol{K_{OW}}$	**Viscosity** (298 K) ln(mPaS)
Cation	**Anion**		
$[DDSPA]^+$	$[TPTP]^-$	9.1	7.8
$[T_{66614}]^+$	$[TMPP]^-$	16.1	10.2
	$[DeA]^-$	12.7	9.7
	$[BA]^-$	10.0	8.6

Four of designed ionic liquids were suggested for experimental tests. The ionic liquid of [DDSP] [TPTP], however, was commercially unavailable and difficult to synthesize. The three other ionic liquids have been experimentally tested.

The obtained experimental results confirmed very high extraction efficiency of Nd from aqueous solution of $NdCl_3$ by all tested ionic liquids [Report for MEXT, 2017; part of the results published at Panigrahi et al. 2016], and thereby confirmed the correctness and effectiveness of the developed theoretical procedures. This encouraged me to perform further investigations on selection of ILs extraction solvents for other common type of Nd salt. Using the previously described procedures, I estimated the potential chemicals of NdF_3 in the selected 900 hydrophobic liquids.

On the base of the obtained results [A9], I found that the same ionic liquids can used for extraction of Nd from aqueous solutions of both salts [A9]. I noted, moreover, high chemical affinity of Nd to another anions: bis(trifluoromethyl)imide $[TFI]^-$, bis(pentafluoroethyl)phosphinate $[PFP]^-$, bissalicylatoborate $[Bscb]^-$, heptafluorobutanoate $[C_3F_7CO_2]^-$, dibutylphosphate $[dbp]^-$, salicylate $[Sal]^-$, and trifluoroacetate $[CF_3COO]^-$ (Tab. 4). I categorized the ions as "second choice" [A9]. **Table**

4. The molecular structures of the ions of "second choice" for liquid-liquid extraction of Nd and Dy selected by COSMO-RS.

Ions of “second choice”	**Molecular structure**
bis(trifluoromethyl)imide $[TFI]^-$	
bis(pentafluoroethyl)phosphinate $[PFP]^-$	
bissalicylatoborate $[Bscb]^-$	
heptafluorobutanoate $[C_3F_7CO_2]^-$	
dibutylphosphate $[dbp]^-$	
salicylate $[Sal]^-$	
trifluoroacetate $[CF_3COO]^-$	

Considering the estimated physicochemical properties of the ionic liquids, and especially their low viscosity and low miscibility with the aqueous phase (Tab. 5), I pointed out on high practical suitability of the new ionic liquids for both: extraction as well as subsequent electrodeposition of these metals.

Table 5. Ionic liquids containing ions of the "second choice" for liquid-liquid extraction of Nd and Dy selected by COSMO-RS.

Ionic liquid		$\mathbf{log_{10}}\boldsymbol{K_{OW}}$	**Viscosity (298 K)** ln(mPaS)
Cation	**Anion**		
$[T_{66614}]^+$	$[TFI]^-$	14.4	5.8
	$[PFP]^-$	13.5	6.8
	$[Bscb]^-$	13.0	8.3
	$[C_3F_7CO_2]^-$	11.4	7.1
	$[dbp]^-$	10.9	9.9
	$[Sal]^-$	10.9	7.6
	$[CF_3COO]^-$	9.6	6.6

Summary

The scientific achievements in the field of separation of metals from industrial waste by method of bromination-evaporation and with a usage of ionic liquids show important scientific and practical technological aspects.

The calculations performed by me allowed for identification the most important thermodynamic properties of all 439 congeners of BFRs and products of their gradual de-bromination. The database, developed be me, is the first ever published in the scientific literature such a complete statement of the thermodynamic properties of BFRs.

Knowledge of the above properties allowed to perform thermodynamic considerations concerning the chemical stability of these compounds, dependency of the stability on the number and location of the bromine substituent, as well as thermodynamic interpretation of the subsequent stages of degradation of BFRs and their transformation into toxic polybrominated dibenzofurans (PBDFs).

The estimated properties help to predict the behavior of these compounds in natural environment. This has a very practical significance, since improper storage or uncontrolled burning of waste containing BFRs and gradual degradation/de-bromination and/or transformation of these compounds many toxic substances causing an environmental hazard can be formed.

The experimental works significantly contribute scientific knowledge regarding fate of the main metals present in EAFD during the thermal treatment of the dust with waste plastic containing BFRs.

Considering the aspect of practical technological implementation, my works indicate on ability to:

(1) practical use of inorganic bromine released during the thermal degradation of BFRs, in particular TBBPA, contained in the waste plastics,

(2) practical recovery of significant amount of zinc and separation of lead from iron-reach residue of EAFD. Very important is the fact that the proposed process is highly effective at extremely attractive temperature, ie. 2-fold lower than that required by Waelz process.

The proposed thermal treatment of waste plastic allows additionally for (i) recovery of their high caloric value and (ii) leads to effective reduction of the weight and the final volume of waste requiring disposal.

The proposed co-combustion, under controlled conditions, of plastic waste with metals-rich EAFD can bring additional benefits in the form of:

(i) simultaneous processing of two groups of wastes in a single process,

(ii) obtaining an iron-rich solid residue possible to re-use in the steel industry,

(iii) utilization of inorganic bromine which otherwise causes corrosion problems of incineration installations.

Due to the growing amount of BFRs-containing waste generated in the world, there are favorable conditions for long-term supply of plastic wastes. And, though there are many methods of disposal of the plastics (mechanical recycling, stock recycling, pyrolysis, gasification, combustion with/without energy recovery), the treatment thermal with energy recovery is the most appropriate method for disposal of heterogeneous plastics.

Due to significant importance, the proposed process of recovery of metals from EAFD by bromination-evaporation has been covered by patent protection in Poland.

The scientific and practical importance is also obvious for the research concerning selection of effective ionic liquid extractants for separation of rare earth metals. The selection method developed be me, is the only published in the scientific press comprehensive tool for *a priori* selection of the effective ILs (without the need for costly and time-consuming experimental tests).

Experimentally confirmed effectiveness of the method developed by my opens the possibility to apply the method for novel applications, ie. studying the ILs extract solvents of any other metals, or any other chemicals.

For example, after selection, with the use of the above procedure, ion (or identification its chemically active molecular group) responding for the extraction properties, future applicant may be tempted for selection or modification of the counter-ion (having no direct impact on the process) which will change properties of the ionic liquid (such as viscosity, affinity for water, electrochemical conductivity) to desired level.

Extremely promising "*a priori*" application of the procedure is for studying impact of different conditions: temperature, pH, chemical modification of the extracting ion, and mixture of ionic liquids, on extraction efficiency.

5. Description of other scientific achievements

As previously mentioned, an important area of my research activity was the management of sewage sludge from municipal wastewater treatment plants. I was particularly interested in utilization, in an environmentally sound manner, of high content of organic and mineral fractions of the sludge for soil fertilization and reclamation. I carried out research and wrote a thesis dedicated to this subject during my post-graduate studies at AGH University of Science and Technology,, as well as supported the Polish-American project concerning an integrated plan for sewage sludge management in the Silesian province. In the above studies, the basic criterion for natural utilization of municipal sewage sludge was content of heavy metals in the sludge.

Less explored aspect that could limit the natural use of municipal sewage sludge is content of organic contaminants. In 2001, I took part in the first in Poland studies concerning presence and fate of PCDD and PCDF during municipal wastewater treatment, at the municipal wastewater treatment plant in Zabrze-Śródmieście.

The research concentrated on occurrence of 17 congeners of these toxic substances with chlorine substituents at 2, 3, 7 and 8 i positions, in municipal wastewater, purified effluent, and in samples of sewage sludge taken at different stages of its processing (excess sludge, digested, dewatered).

It was found that the most toxic PCDDs/Fs present in the inflowing wastewater and these formed during wastewater treatment, is absorbed by formed sewage sludge (24 mg I-TEQ/year) and only a small proportion (0.9 mg I-TEQ/year) migrates to the purified effluent.

Finally, it was found that the measured toxicity of the final dewatered sludge, are clearly lower than the limits for natural utilization of sewage sludge in Germany, as well as those proposed by the US Environmental Protection Agency.

My contribution to the above research was discussion of transformation of these compounds in waste water treatment and sludge treatment.

Another achievement covers theoretical predictions of aqueous solubility of 12 chlorobenzenes by COSMO-RS.

The purpose of this study was compilation of a database of solubility of the persistent organic pollutant within the temperature range from 5 to 60 °C, determination of effect of various salts (NaCl,

KCl and $CaCl_2$) and their concentration (0.01-3.5 mol/l) on aqueous solubility of these compounds, and the relationship between the solubility and the molecular structure of chlorobenzenes (number and localization of chlorine substituents).
My contribution to the above work was the theoretical predictions performed with a usage of COSMOtherm. In the year of study (2005), both the COSMO-RS model and COSMO*therm* program, were at the stage of early development and very pioneering applications. Therefore, the predictions required from me prior optimization of the atomic radius of Ca. Accuracy of the theoretical predictions was proven by close similarities of the predicted and measured (measurements were performed using a generator column) and reported solubility data.
The obtained results showed a very high accuracy of the COSMO-RS predictions. It has been shown that an increase in temperature improves the overall solubility of chlorobenzenes. The effect, was negligible for chlorobenzenes at liquid state (increase of temperature by 10 °C increases their solubility by about 0.048-0.059 log), but become significant for solid chlorobenzenes (increase in the solubility by 0.165-0.174 log).
In the case of effect of the salts, the clear decrease in solubilities of chlorobenzenes along with increasing concentration of salts (salting-out effect) has been identified. The biggest fall of solubility have been seen in the presence of Ca ions, the smaller for ions of Na, and the smallest for K. It has been stated that the effect of salt increases with the number of chlorine substituents in the molecule, however, position of chlorine substitution has no significant effect.

Another part of my scientific activity was to provide support to research regarding behavior of lead oxide (PbO) and iron oxide (Fe_2O_3) (the other two main, next to zinc, components of EAFD) and antimony trioxide (Sb_2O_3) (often used in the plastic industry synergist of BFRs) during the thermal treatment of TBBPA.
It was found, in these studies, that both metal oxides clearly accelerated degradation of TBBPA and had inhibiting affect on the formation of char which promoted carbothermic reduction of the unreacted metal oxides (3% PbO and 75% Fe_2O_3) at temperatures above 650 °C (inert atmosphere). Reduced Pb and Fe remained in the solid residue up to 1300 °C.
It has been found, however, that the partial availability of oxygen (5%) counteract a reduction of metal oxides that, under these conditions, completely evaporated (PbO in the temperature range of 840-950 °C), or remained in the solid residue (87% of the initial Fe_2O_3) unaltered.
Detailed investigations carried out with the laboratory furnace revealed that prolonged heating of the mixture at the quasi-atmospheric conditions (Ar + 20% of oxygen) allows lowering the temperature of the complete removal of lead from the solid residue to 650 °C. Application of the above conditions, allowed additionally for complete oxidation of the organic char, not affecting, however, efficiency of the bromination of PbO to PbBr2 (74-80%), and carbothermic reduction or unreacted PbO (13-20%), which in the metallic form completely vaporized from the solid residue.

Studies on Sb_2O_3 have shown that the oxide reacted with HBr evolved during thermal decomposition of TBBPA immediately after initiation of the decomposition, and at temperature overlapping those observed for ZnO. Main product of the reaction was $SbBr_3$, majority of which quickly vaporized, being in this way "lost" for the bromination of the metal.

Another aspect of my work was to explain the behavior of metals (copper, silver, gold) present in the printed circuit board (PCB) during co-incineration with BFRs.
Considering the fact that the polymeric fraction of PCB often contains TBBPA or TBBPADGE, purpose of the study was, to investigate whether the metals present in PCB can react the bromine released during thermal degradation of the BFRs. For the study, the previously proven experimental (thermogravimetric and furnace) and analytical (IC, ICP, GC-MS, XRD, EPMA) methods were used.
It was shown that gold has very high resistance to bromination reaction. In the cases of copper and silver, both metals revealed high susceptibility (extremely high in the case of copper) to reaction with HBr. Demonstrated, therefore, that during the thermal degradation of the polymeric portion of PCBs, some undesirable losses of copper and silver can occur, which in the form of volatile bromides may transfer to fly ash.

I also assisted the experimental work relating to the use of ionic liquids for the extraction of Nd and Dy from aqueous solutions of their salts. My contribution was to propose ionic liquids and the

experimental conditions for research, as well as substantive support for the analysis of the results. In the above mentioned work, very high extraction of Nd from aqueous solution of $NdCl_3$ to the ionic liquids proposed by me.In the case of of [T_{66614}][BA], obtained extraction yield amounted from 62% (in case of high concentration of Nd in the original feed solution) to 98-99% (for low concentration of Nd in the feed solution).
In the case of [T_{66614}][TMPP] from 87-90% to 100% of Nd was transfer from the aqueous phase to the organic phase, respectively. Efficiency of extraction by [T_{66614}][DeA] was even higher, and ranged from 93-95% to 100%, respectively. In the case of the two later ionic liquids, an addition of an organic solvent (toluene) was necessary to initiate transfer of ions to the extracting liquids.

At the moment I am commencing the implementation of a research project on the use of ionic liquids in the removal of perfluorinated organic contaminants from the aquatic environment. This very broad and innovative research project will combine the use of advanced calculation techniques with laboratory tests, and will lead to the development of a practical technology for removing of these contaminants from water using supported ionic liquids membranes based on the selected ionic liquids.

The total *impact factor* of my scientific activity is: 52.517 (number of MNiSW points: 535), and the Hirsch index is 11 (according to *Web of Science* as well as *Scopus*). In my scientific career, I managed or cooperated in 11 research projects (8 of them after obtaining a doctoral degree), I published 19 scientific papers listed in the *Journal Citation Reports* (all after obtaining a doctoral degree), 8 scientific papers not included in the above list (5 of them after obtaining a doctoral degree), 1 book chapter (after obtaining a doctoral degree), 19 peer-reviewed (all after obtaining a doctoral degree) and 60 non peer-reviewed conference materials (58 after obtaining a doctoral degree).
The total number of citations of my works is 220 (according to the Web of Science) and 223 (according to Scopus), while excluding self-citations is 182 and 180, respectively.
I was involved in organization of 6 international conferences. I have been invited to review 16 scientific papers for 11 journals listed in the *Journal Citation Reports*. I was a member of editorial board of a new scientific journal of international scope, in which I am currently the editor in-chief.

A detailed list of all my publications, conference presentations, scientific awards, indicators of scientific achievements as well as information on research projects, international cooperation, educational, editorial and reviewer activity are presented in Appendix 3.

Mariusz Grabda