

Article

Modified Fly Ash-Based Adsorbents (MFA) for Mercury and Carbon Dioxide Removal from Coal-Fired Flue Gases

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Abstract: One of the solid waste produced during the combustion of coal are fly ashes. Disposal challenges and environmental consequences are the results of significant process yield and atmospheric emission of fly ashes. The exact chemical composition of FA depends mainly on the type of utilised fuel and combustion conditions. It consists mainly of chemically stable metal oxides, such as Al_2O_3 , Fe_2O_3 , SiO_2 , CaO , MgO , K_2O , Na_2O and TiO_2 , but its toxicity is related to the possible presence of some trace elements, such as As, Hg, Cd, Se and Cr. The chemical and physical properties of fly ash (e.g., particle size distribution, porosity, and surface area) make it suitable as an adsorbent to remove various impurities from process flows such as flue gas stream. Its suitability for capturing mercury from flue gas was experimentally confirmed due to its abundant supply, particle size, bulk density, porosity, chemical composition and low cost. Hence, the use of fly ash as adsorbents and precursors for the production of heavy metal adsorbents is of great practical importance, as it reduces the cost of mercury capture and alleviates the problems associated with the disposal of solid waste. Studies showed that the chemical components present in fly ash additives could stimulate catalytic oxidative capacity, which increases the adsorption of Hg^0 oxidation and adsorption of both Hg and CO_2 . The presented study analysed fly ashes from different zones of the electrostatic precipitator and verified their suitability for removing impurities from flue gases, i.e., mercury and carbon dioxide. The results outlined modified fly ash as having good Hg and CO_2 removal capabilities. The adsorption efficiency of Hg reached 92% for Hg and 66% for CO_2 , while untreated fly ash reached 67% for Hg and 59% for CO_2 .

Keywords: fly ash; coal combustion; mercury removal; carbon dioxide removal; flue gases purification; low-cost adsorbents



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1. Introduction

The atmospheric cycle of mercury lasts up to a year and is difficult to control due to its significant environmental prevalence, with its atmospheric pathways capable of affecting thousands of kilometres [1,2]. Fossil fuel, municipal or medical waste combustion makes up for 90% of all anthropogenic mercury emissions [3,4], with coal combustion alone forming as a leading factor with half of the emission [2,5]. The annual mercury release is estimated at 1000–6000 Mg, contributing to 30–55% of atmospheric mercury [6–8]. In Poland, the estimated anthropogenic emission is 11.8 Mg, out of which 77% (9.1 Mg) originates from solid fuel combustion. The anthropogenic mercury emission presents a significant hazard for human health and the environment, leading governments worldwide to make meaningful efforts in its control. Mercury is considered a highly toxic and dangerous

pollutant under the Clean Air Act Amendments (CAAA) established by the United States in 1990 and regarded similarly worldwide [8,9]. Moreover, the anthropogenic release of CO₂ is a significant problem as it heavily contributes to global warming [10]. The global average of CO₂ atmospheric content has grown over the past 100 years, with a rise of over 1.6 ppm annually. The atmospheric inventory of this compound is bound to increase as the global emission of fossil fuel-derived CO₂ has reached close to 3 ppm [11]. Therefore, reducing CO₂ emissions will be the most significant industrial challenge of the twenty-first century [12].

In 2011, the United States and Chinese governments introduced legislation designed to control mercury emissions from coal-fired power plants and accelerate developments in mercury control technologies with Mercury and Air Toxics Standards (MATS) and emission standards for air pollutants for thermal power plants (ESAPTPP), which pressed for mercury reduction of about 90% and limitation to 0.03 mg·Nm⁻³, respectively [13–15]. Currently, as part of the implementation of Directive 2010/75/EU (IED—Industrial Emissions Directive), which introduces permissible industrial emissions, the Polish energy sector implements Best Available Technology (BAT) methods with an emission limit of 1–10 µg·Nm⁻³, depending on the fuel used and the boiler capabilities.

CCS (Carbon Capture and Storage) is the most advanced technology for carbon dioxide emissions control. Since the CO₂ separation and capture is the most energy-intensive step in CCS processes, much research aims to improve current technologies or develop new approaches [16,17]. Many materials, such as CO₂ sorbents, are tested. These include, among others, synthetic or natural zeolites [17–21] and activated carbon [22]. However, each material requires different methods of modification or activation in order to obtain better CO₂ sorption properties.

The research in flue gas mercury capture stresses the importance of control over its three observed forms: elemental (Hg⁰), oxidised (Hg²⁺) and particulate matter (Hg_p) form [23–25]. Hg²⁺ is easy to capture with conventional methods, such as wet flue gas desulphurisation (WFGD) systems as it is soluble in H₂O, while Hg_p can be effectively separated using dedusting control units (e.g., fabric filters FF or electrostatic precipitators ESP) [8,15]. On the contrary, Hg⁰ poses a challenge to existing air pollution control devices (APCD) due to its high volatility and low water solubility. Additionally, recent findings on CO₂ capture [26,27] point out that the volatile form of Hg⁰ has a destructive effect on sorbents used for carbon dioxide separation and its removal before the sequestration unit might be needed. Therefore, current research is focused on developing suitable solutions for Hg⁰ separation [28].

Global research on mercury and carbon dioxide adsorption focuses on the use of activated carbon but also on the use of fly ash derived from coal combustion. Many studies show that the composition of fly ashes plays a vital role in the removal of Hg⁰ [2,29] (Yang et al., 2017a; Wang and others 2016a) with flue removal potential up to 60% Hg⁰ using raw fly ash (RFA). The ash composition also plays an essential role with Al₂O₃, TiO₂ and Fe₂O₃, improving adsorption efficiency compared to the adverse effects of CaO and MgO. The iron present in the volatile ash promotes the adsorption of Hg⁰. The usage of halogens and metal oxides to physically and chemically modify affects the efficiency of Hg⁰ removal of fly ash to be at a similar level as AC (activated carbon) [8,28]. Recently, cobalt, manganese and iron oxides were used to modify fly ash to remove Hg⁰ from flue gases [30]. There are findings on the addition of Fe and Mn, which increased the efficiency of the fly ash sorbent in the presence of O₂. Modified fly ash produced by wet impregnation effectively removed Hg⁰ due to its oxidation by enriching the well-dispersed Co₃O₄ surface of the fly ash [31]. AC or halogenated AC is now considered the most effective commercial mercury sorbent. Economic and environmental benefits can be obtained by using fly ashes instead of AC. Fly ash modified by HBr especially adsorbs mercury in the form of HgBr₂ and HgO, while raw fly ash adsorbs types of mercury such as HgCl₂, HgS and Hg⁰ [32]. The article aims to examine the possibility of using raw fly ash and modifying it for Hg⁰ and CO₂ separation from flue gas. The authors of this publication investigated the effectiveness

of removing Hg^0 with both raw and modified fly ash. The fly ashes were enriched in metal ions and halides by the addition of various biosorbents. Metal and halogen ions contained in biosorbents acted as effective active sites, which improved the efficiency of Hg^0 removal. The improvement of the Hg^0 removal performance of modified fly ash over its unmodified counterpart was observed. The authors focused on sorbent selection with the most promising results in capturing CO_2 and Hg with oxidation of the latter. The sorbents were reviewed over several environmental concerns: First, the use of fly ash as sorbents. Secondly, to determine the possibility of using them to purify flue gases from CO_2 or Hg^0 .

2. Materials and Methods

2.1. Sorbents Sampling

The work examined the effectiveness of bituminous coal-derived unmodified and modified fly ashes captured in a 4-zone electrostatic precipitator from a conventional power plant. The fly ashes were sampled from four individual precipitation zones (1–4) and as a mixture from an aggregate vessel. The fly ashes were modified by adding a fine biosorbent (OT-500 or MSC-500) to adjust the fly ash composition with desired, sorptive enhancing components, i.e., Al_2O_3 , TiO_2 , Fe_2O_3 and halides: Cl, Br. The list of obtained sorbent variations used in this study is summarised in Table 1.

Table 1. Characteristics of the analyzed sorbents.

Unmodified Fly Ash (FA)		
I.	FA 10-I-	fly ash from the 1st zone of the electrostatic precipitator (ESP);
II.	FA 10-II-	fly ash from the 2nd zone of the electrostatic precipitator (ESP);
III.	FA 10-III-	fly ash from the 3rd zone of the electrostatic precipitator (ESP);
IV.	FA 10-IV-	fly ash from the 4th zone of the electrostatic precipitator (ESP);
V.	FA 10-AG-	Aggregate fly ash from the collector after electrostatic precipitator (ESP);
Modified fly ash-based adsorbents (MFA)		
VI.	FA 10-III:OT-500/1:1–1:1 [w/w]-	composition: fly ash from 3rd zone of ESP with char sorbent obtained from pyrolysis at 500 °C. (Oxytree);
VII.	FA 10-III:OT-500/1:1–1:1 [w/w]-	composition: fly ash from 3rd zone of ESP with char sorbent obtained from pyrolysis at 500 °C. (Oxytree);
VIII.	FA 10-III:OT-500/4:1–4:1 [w/w]-	composition: fly ash from 3rd zone of ESP with char sorbent obtained from pyrolysis at 500 °C. (Oxytree);
IX.	FA 10-IV:OT-500/1:1–1:1 [w/w]-	composition: fly ash from 4th zone of ESP with char sorbent obtained from pyrolysis at 500 °C. (Oxytree)
X.	FA 10-IV:OT-500/4:1–4:1 [w/w]-	composition: fly ash from 4th zone of ESP with char sorbent obtained from pyrolysis at 500 °C. (Oxytree)
XI.	FA 10-AG:OT-500/1:1–1:1 [w/w]-	composition: a mixture of aggregate fly ash with char sorbent obtained from pyrolysis at 500 °C. (Oxytree)
XII.	FA 10-AG:OT-500/4:1–4:1 [w/w]-	composition: a mixture of aggregate fly ash with char sorbent obtained from pyrolysis at 500 °C. (Oxytree)
XIII.	FA 10-III:MSC-500/1:1–1:1 [w/w]-	composition: fly ash from 3rd zone of ESP with Miscanthus-based char obtained from pyrolysis at 500 °C
XIV.	FA 10-III:MSC-500/4:1–4:1 [w/w]-	composition: fly ash from 3rd zone of ESP with Miscanthus-based char obtained from pyrolysis at 500 °C
XV.	FA 10-IV:MSC-500/1:1–1:1 [w/w]-	composition: fly ash from 4th zone of ESP with Miscanthus-based char obtained from pyrolysis at 500 °C
XVI.	FA 10-IV:MSC-500/4:1–4:1 [w/w]-	composition: fly ash from 4th zone of ESP with Miscanthus-based char obtained from pyrolysis at 500 °C
XVII.	FA 10-AG:MSC-500/1:1–1:1 [w/w]-	composition: a mixture of aggregate fly ash with Miscanthus-based char obtained from pyrolysis at 500 °C
XVIII.	FA 10-AG:MSC-500/4:1–4:1 [w/w]-	composition: fly ash from 4th zone of ESP with Miscanthus-based char obtained from pyrolysis at 500 °C

Miscanthus and Oxytree are biomass-derived sorbents obtained from pyrolysis at elevated temperatures (500 °C). Miscanthus belongs to energy crops and is a common ornamental plant. Oxytree (Paulowniaceae in Vitro 112) is a hybrid tree obtained as a clone of Paulownia elongata and Paulownia fortunei.

2.2. Sorbents Analysis

The sorbents used in the experiment were characterised and prepared based on information obtained from several analyses:

- I. Analysis of particle size with ISO standard [33];
- II. Carbon and sulfur content C and S (ultimate analysis) with the ISO standard [34];
- III. Determination of chlorine content with Energy-dispersive X-ray spectroscopy EDXRF PANalytical Epsilon 3XLE;
- IV. Bromine content with the use of Wavelength-dispersive X-ray Fluorescence (WDXRF);
- V. The porous texture analysis by Surface Area Analyzer Gemini™ V Series;
- VI. Energy-dispersive X-ray Spectroscopy, EDX Oxford X-Max spectrometer-SEM FEI Quanta 200FEG microscope;
- VII. Sample metallic content with Energy-dispersive X-ray spectroscopy EDXRF PANalytical Epsilon 3XLE.

2.3. Mercury and Carbon Dioxide Adsorption System

Figure 1 shows a schematic of a bench-scale furnace with a measurement setup to quantify flue gas mercury capture. The experimental setup consists of a tube furnace (2) with a quartz combustion chamber (3) for solid fuels, control units for temperature (5) and airflow (6). The coal sample was positioned in a boat-shaped ceramic crucible (4) and gradually transported (1) to the centre of the combustion zone—the sorbent contacts exiting flue gases in its dedicated adsorption system with low-temperature reactor (7) that ensures stable sorption conditions. After sorption, the carbon dioxide concentration is measured by an NDIR analyser (8-AAB NDIR Analyser), and the gas is scrubbed with three sets of impingers (9) and analysed for mercury content with an analyser (10-EMP-3). In the first impinger, the mercury Hg^{2+} from flue gas is reduced with a 10% SnCl_2 solution to mercury Hg^0 ; in the second impinger, the flue gas is cleaned out of acidic components with a 10% KOH solution while the third impinger removes moisture.

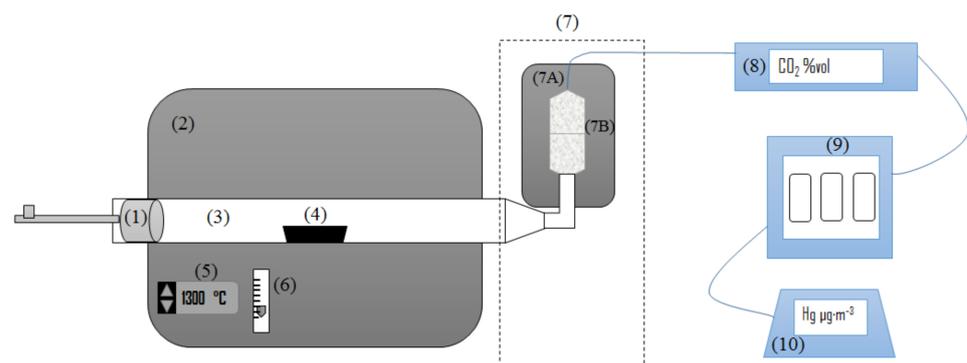


Figure 1. Test stand schematic: (1) metal rod for sample transport; (2) tube furnace; (3) quartz tube; (4) coal sample; (5) temperature regulator; (6) rotameter; (7) adsorption system; (7A) sorbent heater; (7B) glass reactor with sorbent; (8) carbon dioxide analyser; (9) set of impingers; (10) mercury analyser EMP-3.

Determination of flue gas mercury and carbon dioxide concentration was possible after the adsorption system was disengaged. Two fuels for combustion: Sub-bituminous coal and lignite coal underwent ultimate and proximate analysis [34,35], mercury content analysis by atomic absorption spectrophotometry with thermal decomposition followed by amalgamation (DMA-80 Direct mercury analyser; Mile-stone Connect) and chlorine

content analysis under the methodology described in Section 2.2. For the combustion process, sub-bituminous and lignite coal were used. The coal samples were prepared in accordance with the ISO standards [35]. The characteristics of the sub-bituminous coal and lignite are shown in Section 3.2.

3. Results and Discussion

3.1. Sorbent Characteristic

Particle size analysis of fly ash samples from each precipitation zone as well as the aggregate sample was performed by screening in dry conditions. Sieves with mesh diameters of 1 mm, 0.5 mm, 0.2 mm, 0.1 mm, 0.063 mm and 0.032 mm were used in the tests. The results of the analysis are presented in Table 2.

Table 2. Fly ash particulate size distribution.

Sorbent	Granulation (mm)						
	>1	1–0.5	0.5–0.2	0.2–0.1	0.1–0.063	0.063–0.032	<0.032
FA 10-I	0.1	0.3	19.4	44.8	18.2	13.8	3.1
FA 10-II	0.0	0.4	16.9	45.1	18.5	12.5	5.9
FA 10-III	0.2	0.4	16.0	34.1	23.7	22.0	3.5
FA 10-IV	0.3	0.4	10.4	34.7	24.5	27.4	2.3
FA 10-AG	0.1	0.3	13.3	33.9	22.2	24.6	5.5

Fly ashes from 1st and 2nd ESP zones were coarse in general, with 35% *w/w* of fine < 0.1 mm. The granulation of the samples can be observed on SEM FA-10-I and FA-10-II images (Figure 2A,B) along with their high char enrichment. The ashes separated from 3rd and 4th ESP zones had smaller grains with a 0.1 mm fraction constituting between 52.9 and 54.2%, depending on the sample. The aggregate ash contained 52.3% of the 0.1 mm fraction.

FA's determined specific surface (SBET) ranges of several $\text{m}^2 \cdot \text{g}^{-1}$ (see Table 3). For the individual zones of the electrostatic precipitator, this parameter equals $4.4 \text{ m}^2 \cdot \text{g}^{-1}$, $3.8 \text{ m}^2 \cdot \text{g}^{-1}$, $2.9 \text{ m}^2 \cdot \text{g}^{-1}$ and $2.2 \text{ m}^2 \cdot \text{g}^{-1}$, respectively, for 1st, 2nd, 3rd and 4th zones of ESP (decreasing with every stage). Consequently, aggregate fly ash has a minimal surface area among the analyzed samples of $2.1 \text{ m}^2 \cdot \text{g}^{-1}$. The samples did not develop the micro and mesoporous structure.

Table 3. Parameters of the porous structure of analysed fly ashes.

Sorbent	BET Surface Area ($\text{m}^2 \cdot \text{g}^{-1}$)	Micropore Surface Area ($\text{cm}^3 \cdot \text{g}^{-1}$)	Mesopore Volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Total Pore ($\text{cm}^3 \cdot \text{g}^{-1}$)
FA 10-I	4.4	0.006	0.009	0.018
FA 10-II	3.8	0.001	0.010	0.023
FA 10-III	2.9	0.001	0.008	0.018
FA 10-IV	2.2	0.001	0.008	0.018
FA 10-AG	2.1	0.001	0.008	0.018

Raw fly ashes (RFA) were rich in chlorine content (4.3–6.8 wt%), unlike chlorine deficient (0.12 wt%) OT and MSC biosorbents (Table 4). Despite this parameter, the biosorbents had significant oxidizing potential compared to RFA due to several times higher bromine further enhanced by its organic origin. Every sample had a small amount of sulfur with considerably less than 1 wt%.

The presence of various metal oxides such as Al_2O_3 , Fe_2O_3 , TiO_2 , CuO and unburned carbon in the ashes gives promising Hg^0 oxidizing and sorptive properties. The high Al_2O_3 and SiO_2 content with a small addition of TiO_2 and Fe_2O_3 might enhance the adsorption performance, but the limited presence of CaO and MgO can partially inhibit the process. In Table 5 can be see that both the fly ashes and the biosorbents were rich in adsorption promoting metals, but unlike the ash, they contained less MgO and CaO .

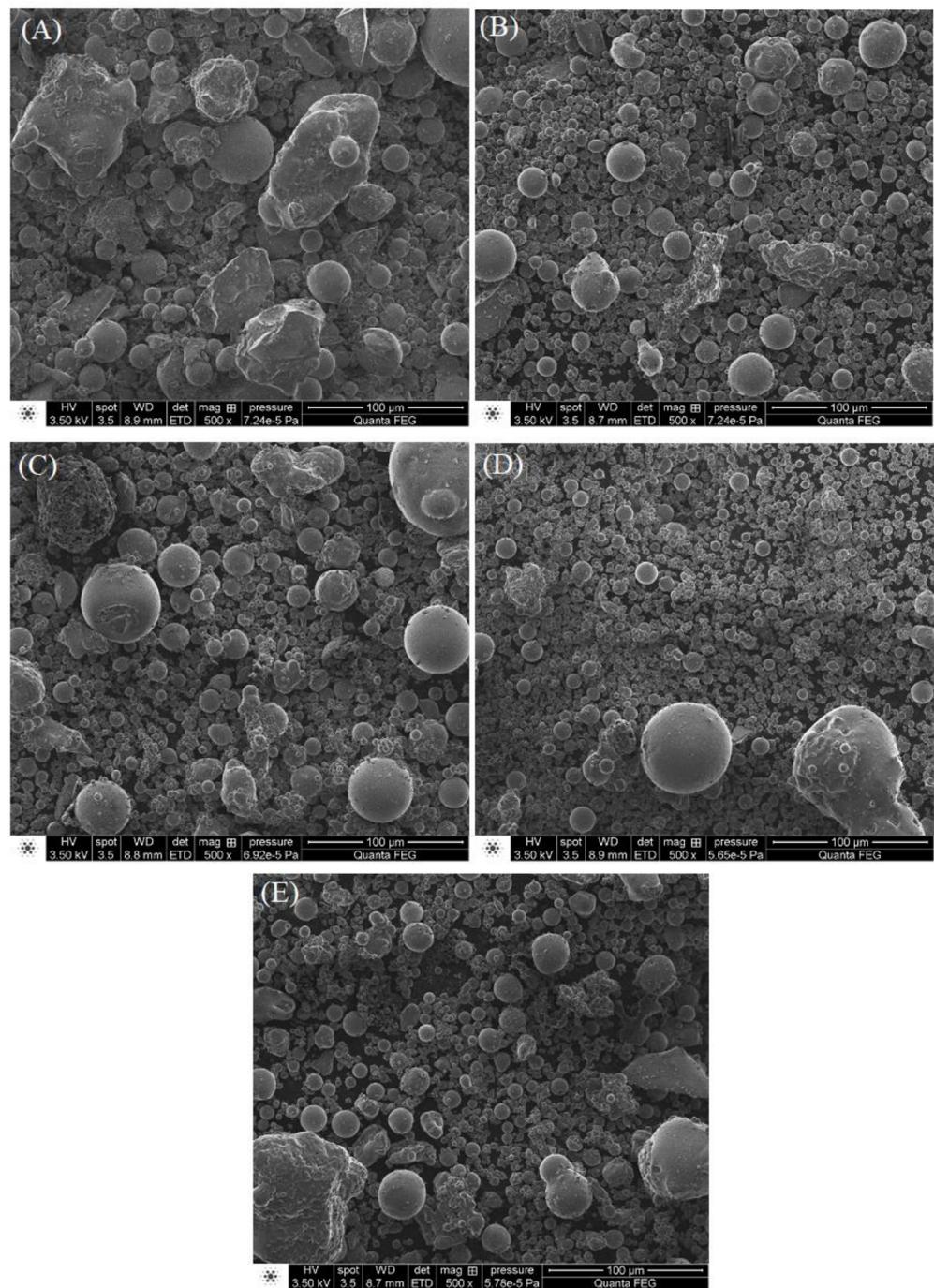


Figure 2. SEM Image (A) FA-10-I (B) FA-10-II (C) FA-10-III (D) FA-10-IV (E) FA-10-AG.

Table 4. Sorption relevant chemical content of the analysed sorbents.

Sorbent	C_{ad} (wt%)	S_{ad} (wt%)	Cl_{ad} (wt%)	Br_{ad} (ppm)
FA 10-I	1.8	0.24	6.81	330
FA 10-II	1.7	0.21	6.47	310
FA 10-III	1.4	0.20	5.23	240
FA 10-IV	1.3	0.37	4.79	170
FA 10-AG	1.3	0.19	4.34	140
OT-500	64.2	0.11	0.13	740
MSC-500	66.8	0.08	0.12	680

Table 5. Inorganic components of tested materials.

Sorbent	Chemical Component (wt%)											
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	SrO	CuO
FA 10-I	1.8	1.4	24.7	46.4	0.3	2.8	3.1	1.2	0.1	5.5	0.0	0.01
FA 10-II	1.9	1.5	24.8	46.2	0.4	2.9	2.9	1.2	0.1	5.5	0.0	0.01
FA 10-III	1.8	1.5	21.9	44.9	0.4	2.9	2.9	1.2	0.1	5.6	0.0	0.01
FA 10-IV	2.0	1.6	20.7	46.2	0.7	2.9	2.9	1.3	0.1	5.6	0.1	0.01
OT-500	1.4	0.43	17.8	40.3	0.2	2.7	0.47	1.5	0.1	6.7	0.0	0.01
MSC-500	1.6	0.13	13.6	39.4	0.2	2.4	0.58	1.4	0.1	7.3	0.0	0.01
SD	0.4 ± 0.6	0.2 ± 0.7	0.7 ± 2.8	0.6 ± 2.8	0.01 ± 0.09	0.1 ± 0.8	0.2 ± 0.8	0.06 ± 0.9	0.01	0.3 ± 1	0.01	0.01

3.2. Characteristic of Combusted Coals

The sub-bituminous coal and lignite sample selected for testing contained 166.0 and 498.1 $\mu\text{g}\cdot\text{kg}^{-1}$ of mercury, respectively (Table 6). The average content of halogens (chlorine and bromine), a supporting factor in the Hg^0 oxidation to Hg^{2+} , reached 3160 ppm of Cl and 15.1 ppm of Br for analysed sub-bituminous coal and 88 ppm Cl and 4.2 ppm Br for lignite. The sub-bituminous coal sample, apart from higher halogen content, had predictably higher carbon content (59.2 to 44 wt%) and slightly higher ash content (25.2 to 21.4 wt%). The lignite sample had a higher amount of every other analysed parameter, such as sulphur content (3.02 to 1.51 wt%), volatile content (39.4 to 24.1 wt%) and moisture (14.9 to 4 wt%). The composition of analysed samples was in agreement with generally established knowledge about solid fuels.

Table 6. Characteristic of the coals used in the experiment (in the air-dry state).

Coal Sample	Ultimate Analysis (wt%)		(ppm)			Proximate Analysis (wt%)		
	C _{ad}	S _{ad}	Cl _{ad}	Br _{ad}	Hg _{ad}	M _{ad}	A _{ad}	V _{ad}
Sub-bituminous	59.2	1.51	3160	15.1	166.0	4.0	25.2	24.14
lignite	44.0	3.02	88	4.2	498.1	14.9	21.4	39.35

3.3. Capture of Mercury and Carbon Dioxide in Flue Gas

3.3.1. Raw Fly Ash (RFA) Hg and CO₂ Capture Efficiency for Flue Gas from Sub-Bituminous Coal and Lignite Combustion

Raw fly ashes differed in their sorption capacity for each ESP sampling zone, with the best result achievable at initial precipitation stages. Both fly ashes from the 1st and 2nd stage of sampling expressed similar mercury capture capabilities with an efficiency of 1.5 to two times higher than other fly ashes, as presented in Table 6. When used on sub bituminous coal-based flue gas, the fly ashes achieved better mercury uptake (reduction from 8.9 to 2.9 $\mu\text{g}\cdot\text{m}^{-3}$ for 1st zone to 3.2 $\mu\text{g}\cdot\text{m}^{-3}$ for 2nd zone) due to lower mercury concentration. The evaluation on lignite-based flue gas showed a lower level of capture (from 17.0 to 9.2 $\mu\text{g}\cdot\text{m}^{-3}$ for both 1st and 2nd zone), but the adsorption equilibrium allowed for more mercury being captured by the samples. The efficiency of fly ash from subsequent zones (3rd, 4th and aggregate) fell below 50% for both sub-bituminous coal (49.4, 41.3 and 32.6% for FA 10-III, FA 10-IV, FA 10-AG) and lignite derived flue (34.1% FA 10-III, 29.4% FA 10-IV, 25.2% FA 10-AG, respectively).

The same relationship was obtained for the effectiveness of reducing the concentration of carbon dioxide. It decreased for fly ash from subsequent ESP zones, with the aggregate sample achieving the worst efficiency. On the other hand, the CO₂ removal efficiency for fly ash of individual ESP zones was more stable between samples and did not fall below 50%. The concentration of CO₂ in the sub-bituminous coal flue gas was 5.4% vol and decreased, depending on the ash sample, to 2.2–2.7% vol (Table 7). In the case of lignite gases, the CO₂ concentration was 14.3% vol and decreased in the range of 6.4–6.9% vol.

Table 7. Stream concentration-based Hg and CO₂ sorption efficiency.

Sorbent	Hg Concentration ($\mu\text{g}\cdot\text{m}^{-3}$)	CO ₂ Concentration (% vol)	Efficiency (%)	
			Hg	CO ₂
Sub-bituminous coal combustion				
Raw flue gas	8.9	5.4	-	-
FA 10-I	2.9	2.2	67.0	59.0
FA 10-II	3.2	2.4	64.1	56.4
FA 10-III	4.5	2.4	49.4	55.2
FA 10-IV	5.2	2.6	41.3	52.3
FA 10-AG	6.0	2.7	32.6	50.4
Lignite combustion				
Raw flue gas	17.0	14.3	-	-
FA 10-I	9.2	6.4	45.8	55.2
FA 10-II	10.0	6.4	41.1	55.0
FA 10-III	11.2	6.5	34.1	54.4
FA 10-IV	12.0	6.6	29.4	53.7
FA 10-AG	12.7	6.9	25.2	51.6

Raw fly ash from 3rd, 4th and FA 10-AG weakened sorptive properties for mercury and carbon dioxide derives from their small specific surface area, less developed pore structure and inferior amount of active sites (see Table 3). Therefore, these three sorbents were modified in the following experiment step to improve their adsorption capacity.

3.3.2. MFA-Based Adsorbents for the Capture of Mercury and Carbon Dioxide in Flue Gas

Fly ash modifications are based on the addition of various oxidant and metal oxide-rich materials resulting in significantly improved adsorption capacity for mercury and carbon dioxide by an increase of its active sites and specific surface area [32]. The analysed studies show that sorbents from raw fly ash achieve a mercury removal efficiency within the broad range of 25–67% and 50.4–59% for carbon dioxide. The addition of biosorbents resulted in a much higher efficiency range of 64.5–92.3% for Hg and 54.1–66.3% for CO₂. The efficiency comparison between raw and modified fly ash is shown in Figure 3. The table with the results, the same as the one with the results for raw fly ash, is presented in Appendix A in Table A1.

The addition of OT-500 uniformly improved the efficiency of fly ash irrespective of the amount of sorbent added (ratio of 1:1 or 4:1), but the result differed between the samples. The general trend followed the results of raw fly ash sorption, with fly ash from 3rd ESP zone resulting in 92% efficiency with Hg concentration drop to $0.7 \mu\text{g}\cdot\text{m}^{-3}$ in comparison to $4.5 \mu\text{g}\cdot\text{m}^{-3}$ of unmodified FA 10-III sample for sub-bituminous coal flue gas (point B). The mercury concentration in lignite-based flue gas decreased to 3.1 and $3.2 \mu\text{g}\cdot\text{m}^{-3}$ after applying FA 10-III:OT-500/1:1 and FA 10-III:OT-500/4:1, which resulted in an efficiency of around 82%.

A slightly worse effect of the same modification was achieved for FA 10-IV and FA 10-AG (Figure 3C,D). For bituminous coal-based flue gas, their effectiveness after modification increased by an average of 50% regardless of the ratio of the mixture. The efficiency of removing Hg from lignite flue gases modified FA 10-IV and FA 10-AG increased by 20 and 15%, respectively.

The addition of MSC-500 biosorbent resulted in mercury removal improvement, but similarly to OT-500 samples, both sorbent loads gave indistinguishable results. This finding shows that the ratio of the fly ash mixture and biosorbent alone did not significantly impact the effectiveness of Hg removal—a small addition of material with an enriched chemical composition is sufficient and should be used in different applications such as carriers for carbon in fertilizers [36–38]. However, the chemical composition of the sorbents seems to differentiate them in mercury capture, as every sample removed close to half of the amount reported for sub-bituminous flue capture of OT-500 based MFA—up to 1.4, 1.9 and

2.4 $\mu\text{g}\cdot\text{m}^{-3}$ of mercury for FA 10-III:MSC-500; FA 10-IV:MSC-500 and FA 10-AG:MSC-500, respectively. Interestingly, such differences were not observed in higher mercury streams generated by lignite flue gas, and the results were identical between both biosorbents.

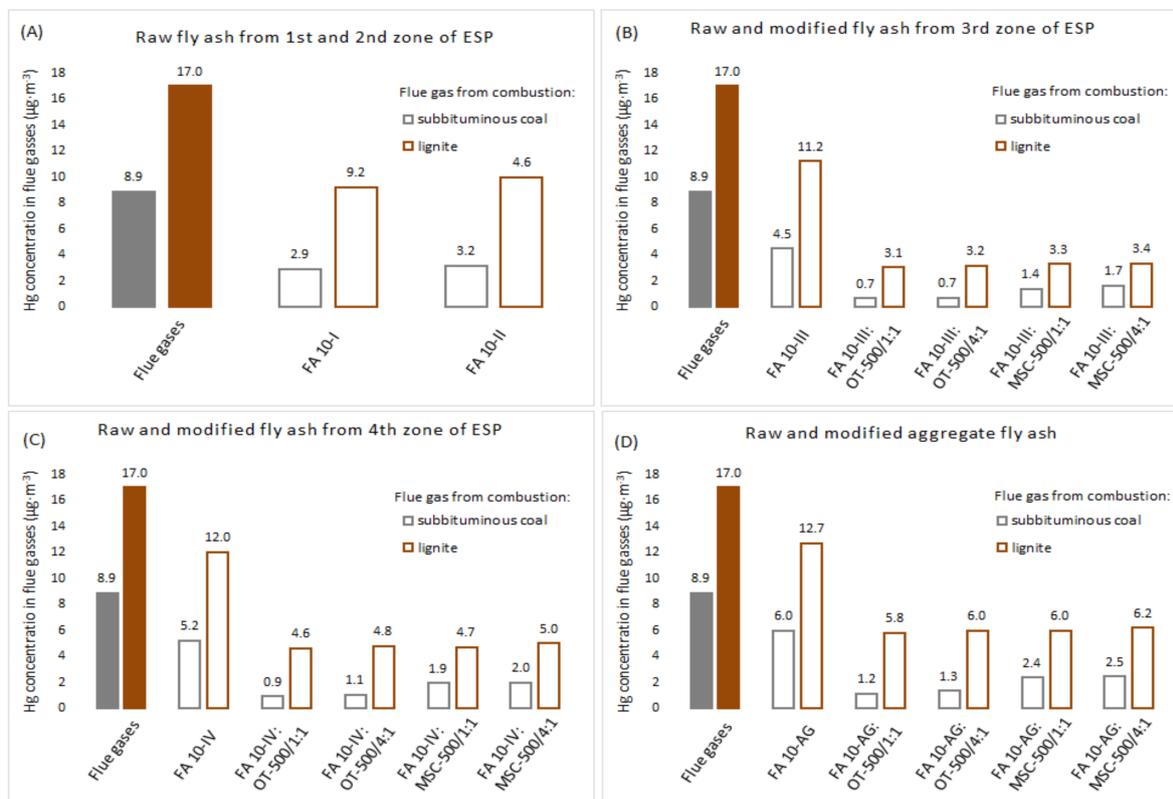


Figure 3. The concentration of mercury in raw flue gas and flue gases cleaned by RFA and MFA from (A) 1st and 2nd zone, (B) 3rd zone, (C) 4th zone, (D) aggregate FA.

The previous observations have outlined that fly ash properties from different precipitation zones have limited influence on their performance as CO_2 adsorbents with an efficiency of around 50% for raw fly ashes. Moreover, the addition of different amounts of biosorbents to the ashes had no significant influence, similar to mercury sorption.

The use of OT-500 sorbent had resulted in the highest increase in CO_2 removal efficiency, although with efficiency gain of up to 11%, it contributed to a much smaller degree than in the case of mercury speciation. Figure 4B shows that fly ashes from the 3rd ESP zone obtained the highest reduction in CO_2 concentration and lowered its concentration from 5.4 up to 2.4% vol for sub-bituminous coal and from 14.3 to 5.6% for lignite (67 and 61% efficiency, respectively). The results of OT-500 sorbent performance for fly ashes from the 4th zone (Figure 4C) and aggregate (Figure 4D) has shown the efficiency regress within subsequent samples. Unlike in mercury sorption, the differences were marginal and did not exceed 3%, notwithstanding the origin of flue gas.

MSC-500 sorbent has shown satisfying removal capabilities for CO_2 , which were comparable but slightly inferior to the results of OT-500 material. The efficiency for fly ashes from different precipitation zones varied only slightly, with a difference of 1 to 5%, depending on the type of flue gas and sample. For sub-bituminous coal-based flue, the results were close to identical between the sorbents, but for lignite-based flue gas, the performance started to slightly weaken, starting from 58% efficiency for 3rd zone modified fly ash up to 54% efficiency for modified aggregate fly ash—only 2% better than its unmodified counterpart. The general capabilities of modified fly ash show that the sequestration of carbon dioxide is primarily dependent on the structure and active sites of the used samples, especially for fly ash.

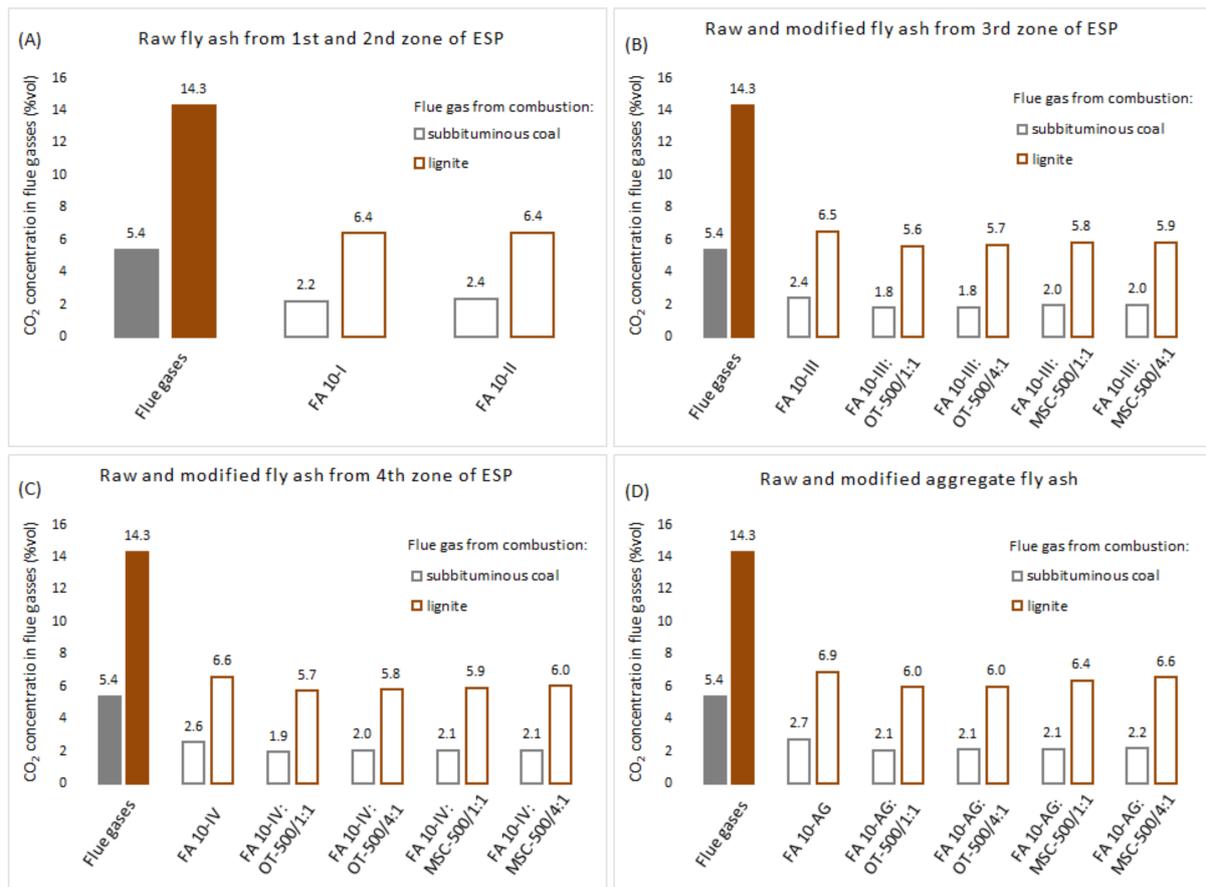


Figure 4. The concentration of carbon dioxide in raw flue gas and flue gases cleaned by FA and MFA from (A) 1st and 2nd zone, (B) 3rd zone, (C) 4th zone, (D) aggregate FA.

4. Conclusions

Currently, AC adsorption technology is the most widely used technology for removing mercury and other pollutants from flue gas. High cost is a crucial factor limiting the adsorption technology for large-scale use in the field of mercury and carbon dioxide removal. The operational conclusions of United States power plants showed that the prices of unmodified AC and brominated AC reached USD 1190/ton and USD 2094/ton, respectively (with mercury removal efficiency 50–90%). Raw fly ash has a meagre cost of capturing Hg and CO₂ due to its wide range of sources, which indicates a good development prospect. The authors of this publication examined the behaviour during Hg and CO₂ removal of raw and biosorbent-modified fly ash and noted the following conclusions:

1. Fly ash from the 1st and 2nd ESP zones is effective in removing both Hg and CO₂. These ashes contain a relatively high content of unburnt carbon, halogens (Cl and Br) and metal oxides such as Al₂O₃, Fe₂O₃, SiO₂, K₂O, Na₂O and TiO₂, which are a factor supporting the oxidation of mercury from Hg⁰ to Hg²⁺;
2. The modified 3rd, 4th and aggregate FA showed a clear improvement in Hg and CO₂ removal efficiency in comparison to unmodified fly ash;
3. Raw fly ash and modified fly ash achieved mercury efficiency of 25–67% and 64.5–92.3%, respectively, and approximately 50.4–59% and 54.1–66.3% CO₂ removal efficiency;
4. Metal and halogen ions contained in the biosorbent, which was an additive to FA, acted as effective active sites, which improved the efficiency of Hg⁰ removal. The increased amount of active sites and specific surface area improved the effectiveness of CO₂ removal, but to a much smaller degree than in the case of mercury removal;

5. The ratio of the FA:OT or FA:MSC mixture did not have a significant impact on improving adsorbents' effectiveness; already, a minor addition (ratio 4:1) clearly improved FA performance.

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Appendix A

Additional Materials for Section 3.3.2—Table 7.

Table A1. Efficacy assessment of MFA for Hg and CO₂ adsorption.

Sorbent	Hg Concentration ($\mu\text{g}\cdot\text{m}^{-3}$)	CO ₂ Concentration (% vol)	Efficiency (%)	
			Hg	CO ₂
Sub-bituminous coal combustion				
Raw flue gas	8.9	5.4	-	-
FA 10-III:OT-500/1:1	0.7	1.8	92.3	66.3
FA 10-III:OT-500/4:1	0.7	1.8	92.0	66.1
FA 10-IV:OT-500/1:1	0.9	1.9	89.4	64.1
FA 10-IV:OT-500/4:1	1.1	2.0	88.2	63.8
FA 10-AG:OT-500/1:1	1.2	2.1	87.0	61.3
FA 10-AG:OT-500/4:1	1.3	2.1	84.9	60.9
FA 10-III:MSC-500/1:1	1.4	2.0	84.1	63.5
FA 10-III:MSC-500/4:1	1.7	2.0	81.2	63.3
FA 10-IV:MSC-500/1:1	1.9	2.1	78.2	61.9
FA 10-IV:MSC-500/4:1	2.0	2.1	77.6	61.4
FA 10-AG:MSC-500/1:1	2.4	2.1	73.5	60.2
FA 10-AG:MSC-500/4:1	2.5	2.2	72.3	59.6
Lignite combustion				
Raw flue gas	17.0	14.3	-	-
FA 10-III:OT-500/1:1	3.1	5.6	82.0	60.7
FA 10-III:OT-500/4:1	3.2	5.7	81.2	60.2
FA 10-IV:OT-500/1:1	4.6	5.7	72.9	59.8
FA 10-IV:OT-500/4:1	4.8	5.8	71.7	59.4
FA 10-AG:OT-500/1:1	5.8	6.0	65.9	58.3
FA 10-AG:OT-500/4:1	6.0	6.0	64.7	58.0
FA 10-III:MSC-500/1:1	3.3	5.8	80.6	59.2

Table A1. Cont.

Sorbent	Hg Concentration ($\mu\text{g}\cdot\text{m}^{-3}$)	CO ₂ Concentration (% vol)	Efficiency (%)	
			Hg	CO ₂
FA 10-III:MSC-500/4:1	3.4	5.9	80.3	59.0
FA 10-IV:MSC-500/1:1	4.7	5.9	72.3	58.7
FA 10-IV:MSC-500/4:1	5.0	6.0	70.6	57.8
FA 10-AG:MSC-500/1:1	6.0	6.4	64.7	55.4
FA 10-AG:MSC-500/4:1	6.2	6.6	63.5	54.1

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