Treatment of Flue Gas in a CO₂ Capture Pilot Plant for a Commercial CFB Boiler

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Abstract: The problem of reducing carbon dioxide emissions from flue gas, particularly from flue gas originating from coal-firing CFB systems, is currently an important challenge. Many centers around the world have tested post-combustion CO₂ capture systems. One of these systems, operated using DR-VPSA adsorption technology (dual-reflux vacuum pressure swing adsorption), was tested under the Strategic Project in Poland. The flue gas in this study originated from a supercritical CFB boiler (460 MW). An important problem involved in capturing CO₂ from flue gas is the occurrence of SO₂ and NOₓ. These substances have a negative effect on the CO₂ adsorption process. In this study, commercial impregnated activated carbon was used to remove SO₂ and NOₓ from CFB flue gas in the pre-treatment section during the tests of a pilot CO₂ capture unit in a large-scale CFB boiler at the Lagisza Power Plant (Poland). The spent activated carbon was analyzed using several different methods (N₂ adsorption–desorption isotherms, SEM-EDX, XRD, FTIR, and TG) to evaluate the efficiency of the operation and life span of the adsorbent used in the SO₂ and NOₓ removal unit. The results demonstrate that using commercial impregnated activated carbon in the pre-treatment section ensures sufficient flue gas purification and the removal of sulfur oxides but remains insufficient for nitrogen oxides.

Keywords: flue gas; CO₂ capture; DR-VPSA; CFB boiler; SO₂/NOₓ removal

1. Introduction

Reducing the emissions of CO₂ and other greenhouse gases contributing to global warming is a global challenge. Among the many proposed CO₂ emission reduction solutions is CCSU (carbon capture and storage/utilization), which enables CO₂ to be captured and then stored or utilized by processing it into a usable product such as methanol using renewable energy sources [1,2]. The most developed and advanced CO₂ capture technologies are amine-based absorption systems such as the large-scale absorption units operating at the coal-fired Boundary Dam power plant in Canada and at the coal-fired Petra Nova power plant in Texas in the United States [2]. Another dynamically developing CO₂ capture technology is the solid adsorbent-based adsorption technique involving vacuum swing adsorption (VPSA) technology [3–9]. To date, at a pilot scale and under real power plant conditions, adsorption units for CO₂ capture on fixed beds have been tested in Japan [4,5], China [6], Australia [7], and Poland [8,9]. According to the tests carried out on all pilot adsorption CO₂ capture units treating real flue gas [4–9], one of the most important factors influencing the effectiveness of CO₂ adsorption is the content of H₂O and other impurities such as SO₂, NOₓ, dust, alkalis, and volatile metals in the flue gas [10–16]. These components have negative effects on the physical adsorbents
used in the adsorption method (activated carbon [4–9,17–19], zeolites [4–9], metal–organic frameworks [20,21], and mesoporous silica [22]), thereby reducing their CO₂ sorption capacity, which affects CO₂ purity and recovery. Meanwhile, many growing present-day recycling methods for CO₂ captured from power plants and other branches of industry require clean CO₂ streams. Moreover, the presence of the above-listed impurities accelerates deactivation of the CO₂ adsorbent, making more frequent replacement of the adsorbent necessary and thus increasing total costs of capturing CO₂ from flue gas. Therefore, it is important to ensure the effective removal of SO₂ and NOₓ from flue gas before the CO₂ adsorption process because both SO₂ and NOₓ can adsorb and/or react with CO₂ adsorption materials [10–19]. Similar to amine-based absorption systems [23], the SO₂ and NOₓ content in flue gas should be ca. 10 mg/Nm³ before the flue gas is sent to the CO₂ adsorption unit, while the limits of SO₂ and NOₓ emissions from flue gas needed for coal power plants in the EU are now 200 mg/Nm³ [24]. As a result, all pilot CO₂ separation units described in the literature comprise pre-treatment sections designed to dry and purify flue gas, which primarily involves the removal of SO₂ and NOₓ before it is sent to the CO₂ capture section. This assignment is impacted by using various methods and adsorbents (Figure 1). Regrettably, there is little information concerning the functioning of these units, their efficiency, and the effectiveness of adsorbents used to remove SO₂ and NOₓ [4,7]. For flue gas drying alongside the removal of SO₂ and NOₓ in a pilot VPSA CO₂ capture unit, Wang et al. [6] proposed a pre-treatment unit consisting of a two-column TSA (temperature swing adsorption) module in which 156 kg of alumina was used as the adsorbent [6]. This adsorbent was also used by Ishibashi et al. as a packing material in a PSA (pressure swing adsorption) unit employed as the pre-treatment section for flue gas drying and additional SO₂ removal in an adsorption CO₂ capture unit [4,5]. Studies demonstrated that in addition to adsorbing moisture, the applied alumina also co-adsorbed CO₂. As a result of these tests, it was observed that in the primary stage, alumina acted as a moisture absorbent and also captured SO₂ in the form of sulfuric acid and aluminum sulfate, which was found in an adsorbent taken from the bottom part of the adsorption column. It was demonstrated that this result did not affect dryer efficiency. The SO₂ removal was so effective that no SO₂ accumulation was observed in the CO₂ adsorbent removed after 2000 h of use in a PTSA/PSA adsorption unit installed to capture CO₂. These studies confirmed that the applied alumina worked as both a moisture adsorbent and as a filter protecting against SO₂.

![Diagram](image-url)

**Figure 1.** Pre-treatment sections in global pilot adsorption CO₂ capture units (PTSA: pressure temperature swing adsorption; PSA: pressure swing adsorption; VSA: vacuum swing adsorption; VPSA: vacuum pressure swing adsorption; DR-VPSA: dual-reflux vacuum pressure swing adsorption).
On the other hand, in the solution proposed by Qader et al. [7], no separate unit for the drying and removal of SO\(_2\) and NO\(_x\) from flue gas was used, but the pre-treatment unit’s function was affected by an adsorber column with multiple layers, removing H\(_2\)O/SO\(_2\)/NO\(_x\) in the first layer of the adsorbent and CO\(_2\) in the second layer [7]. Multi-layer adsorbents were applied in this solution: The first layer consisted of adsorbents used to remove water and SO\(_2\)/NO\(_x\) from flue gas, and the second consisted of adsorbents selective to CO\(_2\). This system’s functionality demonstrated that SO\(_2\) and NO\(_x\) not captured from flue gas may cause blower corrosion induced by generated sulfuric acid. Thus, the elimination of SO\(_2\), NO\(_x\), and water from flue gas is required in the commercial use of adsorption installations for capturing CO\(_2\) because these impurities may negatively affect the functionality of the installation elements. A different solution was employed in a Polish installation [8] where the pre-treatment section consisted of three different subsections: a cooling and heat recovery section, desulfurization and NO\(_x\) removal adsorbents, and a drying section. To date, only in this solution were far flue gas drying and the removal of SO\(_2\) and NO\(_x\) carried out in separate sections. Another innovation was to use activated carbon impregnated with potassium hydroxide and potassium iodide for the simultaneous removal of SO\(_2\) and NO\(_x\) [8]. This adsorbent was chosen because impregnated activated carbon was proposed, primarily for the simultaneous removal of SO\(_2\) and NO\(_x\). While the adsorption of gases on activated carbon is predominantly driven by physisorption, that of the modified carbon surface is driven by both physisorption and chemisorption. Modification of the AC surface is necessary to improve attraction between the adsorbent and target gases, resulting in a higher adsorption capacity of gases, especially at low gas concentrations in the flue gas. As an impregnating substance, KOH is known to have an excellent selective adsorption capacity for acid gases. An AC upgraded by impregnating it with KOH and KI promoted chemisorption with SO\(_2\) and NO\(_x\) [25–30].

Moreover, no data are available on the use of activated carbon impregnated with KOH/KI for the simultaneous removal of SO\(_2\) and NO\(_x\) in pilot adsorption CO\(_2\) capture installations under the operational conditions of large-scale CFB facilities. Valuable pilot plant data from commercial CFB units are presented in this work. Only a few studies have been devoted to the impacts of impurities such as SO\(_2\) and NO\(_x\) on CO\(_2\) adsorption by VSA (vacuum swing adsorption) [13] in the extant literature. Considering this factor, the present article focuses on assessing the efficiency of applied adsorbents in the removal of SO\(_2\) and NO\(_x\) from flue gas prior to the CO\(_2\) removal process at the Lagisza Power Plant. To assess the efficiency of using impregnated activated carbon in pre-treatment units to remove SO\(_2\) and NO\(_x\) from CFB (circulating fluidized bed) flue gas, a comprehensive analysis of the adsorbents was carried out before and after their use in the desulfurization and NO\(_x\) removal section in a pilot adsorption (DR-VPSA) CO\(_2\) capture unit under typical flue gas conditions. Studies of this type have not been reported in the CFB literature. Many articles discuss and focus on H\(_2\)O impacts on CO\(_2\) sorption in adsorption installations, but there are no detailed analyses regarding effective SO\(_x\) and NO\(_x\) removal from flue gas. The available literature rarely reports real CFB flue gas treatments. Studies of this type would not only help us understand the principles of impurity adsorption and the efficiency of applied adsorbents but would also provide valuable data for the design of adsorption-based demonstration CO\(_2\) capture installations. The purpose of the current research was to understand simultaneous SO\(_2\) and NO\(_x\) adsorption on impregnated activated carbon at the stage of CFB flue gas pre-treatment in post-combustion CO\(_2\) capture. Evaluation of the desulfurization/denitrification mechanism was performed through spent activated carbon post-analysis.

2. Experimental Section

2.1. Pre-Treatment Section in a Pilot-Scale DR-VPSA Carbon Capture Unit

In 2015–2016, under the Strategic Project financed by NCBiR (the National Centre for Research and Development) in Poland, research was carried out on post-combustion CO\(_2\) capture in a pilot DR-VPSA mobile unit located at Tauron Wytwarzanie S.A.—The Lagisza
Power Plant in Poland. The flue gas originated from the world’s first supercritical CFB boiler (460 MW). The mobile CO₂ capture unit consisted of a flue gas pre-treatment section and a carbon dioxide separation section (four-bed DR-VPSA) (Figure 2). In the proposed solution, a complex pre-treatment section was used for the first time and compared to other pilot CO₂ adsorption units [4–7]. The pre-treatment unit consisted of heat exchangers, an isothermal absorber, a deSO₂ and deNOₓ adsorber, and a glycolic gas dehydration system. The CO₂ separation unit consisted of four two-section adsorbers [8]. Detailed information about the mobile pilot DR-VPSA unit and the performed tests is available in previous studies [8,9]. The present article focuses only on the functionality of desulfurization and the NOₓ removal adsorber, which is an element of the flue gas pre-treatment section. More specifically, this study focuses on evaluating the desulfurization/denitrification mechanism through spent activated carbon post-analysis.

Figure 2. The scheme of the pilot DR-VPSA unit including the locations of the AC sample retrieval for analysis purposes (1, 2: flue gas drawing locations).

Before the flue gas generated in Lagisza Power Plant was sent to the pilot four-bed DR-VPSA unit, the following impurities were removed from the gas at the plant: SO₂, using a dry desulfurization method, and NOₓ, using selective, non-catalytic reduction. The resulting average SO₂ and NOₓ content in the flue gas from the CFB boiler was as follows: SO₂ of 154.6 mg/Nm³ and NOₓ of 179.8 mg/Nm³ [8]. These content levels satisfy the applicable emission standards for these gases but remain too high for CO₂ capture units. As a result, the CO₂ capture installations need a pre-treatment section to reduce the SO₂ and NOₓ from the flue gas to ca. 10 mg/Nm³. Effective SO₂ and NOₓ removal in this section is essential because this removal affects the purity of the CO₂ captured in the CO₂ separation unit [9], which is important for recycling the obtained CO₂ stream. Many of the proposed recycling methods require a high-purity CO₂ stream. For example, NOₓ can be a problem in the CO₂ stream if the stream is intended to be used in the food and beverage industry.

2.2. Characterization of the Adsorbent Used in the deSO₂ and deNOₓ Adsorber

Activated carbon (AC-P) Airpel 10 impregnated with potassium iodide KI (ca. 2 wt.%) and KOH (ca. 3 wt.%) manufactured by DESOTEC. Activated Carbon was used for the simultaneous removal of SO₂ and NOₓ in the flue gas pre-treatment section pilot DR-VPSA CO₂ capture unit. This carbon (130 kg) was used as packing in the deSO₂ and deNOₓ adsorber (Figure 3). The activated carbon (AC-P) in this study was granulated activated carbon produced from anthracite with a pellet radius of >2.36 (99% mass), density of 520 kg/m³, water vapor capacity of 40.1%, and a highly developed surface of 959 m²/g. While the adsorption of gases on porous activated carbon is driven primarily by physical adsorption, in the case of a modified carbon surface (KOH), the adsorption of gases is driven by both physical adsorption and chemisorption with a chemical reaction between the surface function groups and adsorbed gases. AC surface modification is necessary to
improve the pull between the adsorbent and gases, especially when the gas concentration in flue gases is low. This type of modification is required to increase the alkalinity and general chemistry of the carbon surface under the pull of strongly polarized SO$_2$ gas. Potassium iodide performs the role of an “oxygen carrier”. The deSO$_x$ and deNO$_x$ adsorber was designed to reduce SO$_2$ to ca. 10 mg/Nm$^3$ and NO$_x$ to 40 mg/Nm$^3$. The deSO$_x$ and deNO$_x$ adsorber functioned continuously for 808 h in the pilot CO$_2$ capture installation (DR-VPSA) under the operational conditions of a large-scale CFB facility. The activated carbon (AC-P) samples were taken for analysis afterwards. Replacement of the AC-P sorbent that filled the deSO$_x$/deNO$_x$ adsorber was not necessary after 808 h of DR-VPSA operation because no increase was observed in the SO$_2$ concentration at the outlet of the column. If necessary, regeneration of the spent adsorbent was carried out using the activated carbon producer (DESOTEC Activated Carbon). Figure 3 shows the locations where activated carbon samples were retrieved for the tests (bottom, middle, and top of the adsorption column).

![Image](image_url)

**Figure 3.** Retrieval locations for the activated carbon AC-P used as packing for the deSOx and deNOx adsorber in the pilot DR-VPSA CO$_2$ capture unit.

The spent activated carbon was analyzed using different methods (N$_2$ adsorption–desorption isotherms, SEM-EDX, XRD, FTIR, and TG) to evaluate the desulfurization/denitification mechanism, efficiency of operation, and durability of the adsorbent used in the deSO$_x$ and deNO$_x$ adsorber. The impregnated activated carbon AC-P was also characterized before being used in the deSO$_x$ and deNO$_x$ adsorber. A Leco Elemental Analyser CHNS was used to assess the AC-P chemical composition. The porous properties of AC-P activated carbon after 808 h of use in deSOx and deNOx adsorber were assessed based on the N$_2$ adsorption–desorption isotherm at −196 °C using a Micromeritics model ASAP 2010. Prior to the measurements, the sample was outgassed at 473 K under an N$_2$ flow for at least 3 h. The BET method was then used to determine the specific surface area of the AC-P, and the BJH method was used to assess the pore-size distribution. Before and after adsorption, a surface chemical analysis of the sample was performed using SEM (EVO-40 Series, Carl Zeiss SMT electron microscope equipped with an energy dispersive X-ray spectroscope).
FTIR (Nicolet 6700 spectrometer), and XRD (X-ray diffractometer Panalytical X’PERT PRO). TG was performed using a Mettler TGA/DSC1 thermal analyzer. About 10 mg of the activated carbon was heated at 20 °C min⁻¹ to 1000 °C with a flow ratio of nitrogen equal to 50 cm³ min⁻¹. The online analysis of SO₂ and NOₓ concentrations in the flue gas was carried out during the measuring tests of the pilot DR-VPSA unit installation with real CFB flue gas at the Lagisza Power Plant to complete the information obtained from analyzing the physicochemical properties of the impregnated activated carbon (AC-P) before and after its use in the deSOₓ and deNOₓ adsorber. The concentration of SO₂ and NOₓ gases was registered before (point 1) and after the deSOₓ and deNOₓ adsorber (point 2) to continuously monitor the effectiveness of the process involving SO₂ and NOₓ removal from the flue gas (Figure 2). During testing, gas samples were taken continuously using a multiplexer and directed to an analyzer equipped with an FTIR sensor to measure the SO₂ and NOₓ concentrations. This analysis was also carried out in the CO₂ separation section to assess the effect of these impurities on the working efficiency of the CO₂ adsorbent and on the captured CO₂ purity. Detailed information on the results obtained in the CO₂ separation section is available in [9]. The present article focuses only on analyzing the SO₂ and NOₓ content in flue gas at the inlet to the deSOₓ and deNOₓ adsorber and at the exit from the deSOₓ and deNOₓ adsorber.

3. Results and Discussion
3.1. Chemical Composition of the Spent Activated Carbon

The elemental chemical compositions of the fresh and used impregnated activated carbon AC-P in desulfurization and the NOₓ removal adsorber are shown in Table 1. The primary differences in constitution between the fresh AC-P and the three used AC-Ps (retrieved from the bottom, middle, and top of the desulfurization unit) were their sulfur contents. Samples of used AC-P taken from the desulfurization unit had a notably higher S content (from 0.98 to 4.14 wt.%) compared to the fresh AC-P (0.29 wt.% S), which led to effective SO₂ adsorption from the flue gas under treatment, primarily in the lower part of the deSOₓ and deNOₓ adsorber (used AC-P (1)). Analysis of chemical composition also demonstrated that AC-P impregnated with KOH/KJ, which was used in the deSOₓ and deNOₓ adsorber, did not adsorb nitric oxides from treated gas and was not effective in this regard. In the samples of used AC-P retrieved from the deSOₓ and deNOₓ adsorber, no N content was observed to be higher than that in fresh AC-P.

| Adsorbent               | Elemental Composition |
|-------------------------|-----------------------|
|                         | C, wt.% | H, wt.% | N, wt.% | S, wt.% | Other, O wt.% |
| fresh AC-P              | 72.34   | 1.80    | 0.86    | 0.29    | 24.71         |
| used AC-P (1)—bottom   | 63.16   | 2.66    | 0.67    | 4.14    | 29.37         |
| used AC-P (2)—middle   | 66.81   | 2.56    | 0.53    | 2.75    | 27.35         |
| used AC-P (3)—top      | 69.86   | 2.44    | 0.73    | 0.98    | 25.99         |

3.2. Porous Structure of the Spent Activated Carbon

By analyzing data on the porous structure (Table 2) of the activated carbon before and after 808 h of use in the deSOₓ and deNOₓ adsorber, it was possible to observe changes in the specific surface area and volume and surface area of the pores. The specific surface area of AC-P after 808 h of use in the adsorber decreased for the used AC-P by 23.21%–42.11% (depending on the location of AC-P retrieval in the deSOₓ and deNOₓ adsorber) compared to fresh AC-P (whose specific surface was 959 m² g⁻¹). The volume of pores also decreased by 19.52% to 43.91% (depending on the location of AC-P retrieval in the deSOₓ and deNOₓ adsorber). Moreover, the total area of pores in all spent AC-Ps decreased by 22.54–37.92% (Table 2). The spent samples had smaller specific surface areas and volumes of micropores, likely due to the presence of SO₂ adsorbed from the polluted flue gas and perhaps from
other impurities such as dust. The SO₂ adsorption process resulted in a decrease in the BET surface areas and pore volume of the activated carbon materials, indicating a blocking of pores due to clusters of new stable ionic crystals of K₂SO₃ and K₂SO₄. The degree of reduction in terms of both the area and the pore volume was the greatest for the used AC-P (1) taken from the lower part of the desulfurization unit. This used AC-P adsorbed the largest amount of SO₂ from the flue gas.

Table 2. Porous properties of the fresh and used impregnated activated carbon AC-P.

| Sample           | BET Surface Area, m² g⁻¹ | Total Pore Volume, cm³ g⁻¹ | Total Pore Area, m² g⁻¹ |
|------------------|--------------------------|----------------------------|------------------------|
| fresh AC-P       | 959.00                   | 0.41                       | 739.30                 |
| used AC-P (1)—bottom | 555.20                   | 0.23                       | 459.03                 |
| used AC-P (2)—middle | 692.13                   | 0.31                       | 572.67                 |
| used AC-P (3)—top | 736.46                   | 0.33                       | 515.95                 |

Sulfur presence was also confirmed by analyzing the chemical composition of the samples (Table 1). Figure 4 presents the nitrogen adsorption–desorption isotherms (Figure 4a) and pore-size distributions (Figure 4b) for the activated carbon AC-P samples before and after use in the deSOₓ and deNOₓ adsorber. The adsorption/desorption isotherm of fresh AC-P was a type I isotherm, which confirmed the adsorbent’s microporosity with a large number of mesopores, as demonstrated by the hysteresis loop starting at relative pressure (p/p₀) over 0.35. The adsorption/desorption isotherms of the used AC-P presented the same shapes, and differences in relation to fresh AC-P mainly applied to the volume of adsorbed nitrogen (Figure 4a).

Figure 4. Cont.
Figure 4. Nitrogen adsorption–desorption isotherms (a) and pore-size distributions (b) for activated carbon samples: fresh AC-P, used AC-P (1), used AC-P (2), and used AC-P (3).

This was demonstrated by the behavior of the porous structures of the used AC-P samples after 808 h of use in the desulfurization unit. As shown in Figure 4b, minor changes can also be observed in the pore-size distributions for the activated carbon AC-P samples, both fresh and used. This confirms the presence of minor changes in the porous structures of the AC samples after 808 h of using them to remove sulfur and nitrogen from flue gas before delivering the gas to the adsorption installation for CO₂ separation.

3.3. Microstructure of the Spent Activated Carbon

The presence of sulfur in the spent activated carbon AC-P was confirmed by SEM-EDX analysis, according to which the sulfur content was a maximum of 14.0 wt.% for used AC-P (3) retrieved from the adsorber top, 14.92 wt.% for used AC-P (2) retrieved from the adsorber middle, and 20.29 wt. % for used AC-P (1) from the adsorber bottom.

Figure 5 shows SEM photographs and the results of the SEM-EDX chemical constitution analysis on the surface of the impregnated activated carbon (both fresh and used) in the deSO₄ and deNO₃ adsorber. The observation of the microstructure in the tested AC-P samples confirmed the occurrence of new structures as a result of the use of the samples in the adsorber. Photographs of the spent AC-P showed crystals of sulfate and potassium sulfite formed as a result of SO₂ sorption. Most of the K₂SO₄ crystals were formed in the bottom of the desulfurization unit (used AC-P (1)), as demonstrated by the SEM photographs (Figure 5b) showing the greatest amount of potassium sulfate crystals. This result was also confirmed by analyzing the chemical composition on the surfaces of the activated carbons, which showed higher sulfur and potassium (K₂SO₃ and K₂SO₄) content compared to fresh AC-P in the AC-P samples retrieved after 808 h of use in the adsorber.

3.4. Surface Chemistry of the Spent Activated Carbon

Characterization of the FTIR spectra for sample surface chemistry was carried out to obtain information on changes in the functional groups on the AC-P surface before and after desulfurization and denitrification. Analysis of the FTIR spectra for fresh AC-P and AC-P after use in the adsorber, as presented in Figure 6, confirmed surface changes in the used AC-P due to SO₂ adsorption.
Figure 5. SEM-EDX analysis of activated carbon (fresh and used) in the deSO$_x$ and deNO$_x$ adsorber: (a) AC-P; (b) used AC-P (1); (c) used AC-P (2) and (d) used AC-P (3).

Figure 6. FTIR profiles of impregnated activated carbon: fresh and after use in the deSO$_x$ and deNO$_x$ adsorber: fresh AC-P, used AC-P (1), used AC-P (2), and used AC-P (3).

No observed changes indicated NO$_x$ adsorption. The fresh and used AC-P spectra showed characteristic peaks related to -OH vibrations at 1650 cm$^{-1}$ and 3500 cm$^{-1}$ due to the presence of the basic group -OH (originating from KOH and moisture). Moreover, at the 1800–1690 cm$^{-1}$ wavelength, we observed a peak generated by the ketone group C=O and at 1630 cm$^{-1}$ from the aromatic group C=C. Below 1600 cm$^{-1}$, we observed low-intensity peaks from the C=O, C-O, and -OH groups. Extra peaks appeared in the spectra of all used AC-P samples retrieved from the deSO$_x$ and deNO$_x$ adsorber, which confirmed changes on the surfaces of the spent activated carbons. The signals at 1150 cm$^{-1}$ could be linked to sulfates generated after SO$_2$ adsorption (the strong band/spectrum of the
-OH group belonging to the -SO-OH group was generated during SO₂ adsorption on the AC-P at 3435 cm⁻¹, the band at 1159 cm⁻¹ originated from the –SO₃⁻ group, and the strong band at 1113 cm⁻¹ originated from the -O-SO₃⁻ group [28]. During the analysis of SO₂ adsorption on activated carbon with potassium hydroxide activation, many of the same groups were observed by Lee et al. [28]. No groups indicating the formation of nitrates were found on the surface of the used AC-P. Moreover, a weak band of the -SO₂⁻ group appeared at 984 cm⁻¹. However, as emphasized by other authors [28], low-intensity peaks that induce microscopic changes via functional groups generated through SO₂ adsorption might become hidden or overlap and thus would not be observed. To sum up, during SO₂ adsorption, activated carbon impregnated with KOH works as a selective site of adsorption, with the OH⁻ groups guaranteeing basic atmosphere and K⁺ ions facilitating stable SO₂ adsorption on carbon. Due to potassium, the chemicals created on the surface during adsorption include stable ionic crystals such as K₂SO₃ and K₂SO₄. This is because potassium is highly reactive and cannot exist as a single element; instead, potassium exists in chemical compounds [28]. Previous studies on the properties of carbon surfaces after SO₂ adsorption indicate that strong chemical interactions between KOH and SO₂ largely depend on the impregnated carbon’s surface chemistry.

3.5. Stability of the Spent Activated Carbon

Based on the information for the surface functional groups obtained from the FTIR analysis, the presence of adsorbed substances on the used AC-P was also examined using XRD analysis. The XRD analysis allowed us to identify the substances formed on the surface of the activated carbon after SO₂ adsorption. Figure 7 shows the XRD spectra for fresh and used AC-P. For fresh AC-P, a high-intensity peak (2θ = 26.5) was observed. This peak was not seen on any of the used AC-Ps. This peak may indicate the presence of potassium and basic OH ions (AC impregnated with KOH) on the external surface of fresh AC-P that disappeared after SO₂ adsorption. The XRD spectra of all the used AC-Ps indicated the presence of K₂SO₄ generated as a result of a reaction between sulfur oxides and potassium hydroxide (high-intensity peak at 2θ = 30.7), whereas high-intensity peaks at 2θ = 21.24, 29.7, 30.74, and 43.36 as well as small intensity peaks at 35.8 and 37.04 were observed in all the samples after SO₂ adsorption.

![Figure 7](image_url)

**Figure 7.** The XRD spectra of activated carbon (fresh and after use in the deSOₓ and deNOₓ adsorber): fresh AC-P, used AC-P (1), used AC-P (2) and used AC-P (3).
Figure 8a,b shows the TG and DTG curves of activated carbon (fresh AC-P and AC-P after use in the deSO₂ and deNOₓ adsorber) under an inert atmosphere (N₂). As shown in Figure 8a, each sample was characterized by varying the mass loss during the experiment. The greatest mass loss was observed for activated carbon with AC-P (1) after use in the deSO₂ and deNOₓ adsorber. The loss amounted to 35%, whereas fresh AC-P’s mass loss was 20%. As indicated by the TG/DTG curves (Figure 8a,b), two types of mass loss were observed in the fresh AC-P sample. The first type of mass loss was due to the desorption of physically adsorbed water. The second type of mass loss (200–1000 °C) resulted from the slow thermal decomposition of the surface functional groups with low stability and the least thermally stable carbon structure.

![Graph](image)

**Figure 8.** TG (a) and DTG (b) curves of activated carbon (fresh and after use in the deSO₂ and deNOₓ adsorber): fresh AC-P, used AC-P (1), used AC-P (2), and used AC-P (3).

Different situations were observed for all spent AC-P-activated carbon. As indicated by the TG/DTG curves (Figure 8a,b), four types of mass loss were observed in the spent AC-
P samples. The first type of mass loss (30–200 °C) was due to the desorption of surface water. The second type of mass loss (200–400 °C) resulted from the removal of water from the pores of the adsorbent. The third type of mass loss (440–650 °C) was due to the desorption of sulfur. The fourth type of mass loss (>650 °C) resulted from the decomposition of potassium sulfate. All completed analyses demonstrated that the mechanism of deep flue gas purification on the activated carbon using AC-P involved the reaction of SO₂ to K₂SO₃ and, through oxidation of SO₂ to SO₃ and adsorption, a reaction to K₂SO₄. The presence of these compounds was confirmed by XRD, SEM-EDX, and TG analyses. However, the presence of nitrogen oxide removal products was not observed, indicating that nitrogen oxides, especially NO, were not oxidized in the desulfurization unit to N₂O₅ and N₂O₄ and thus did not react with KOH to produce potassium nitrates and nitrates (KNO₂, KNO₃). The FTIR, XRD, SEM-EDX, and TG analyses also did not confirm the existence of these compounds. A previous study carried out by the present authors also confirmed that NOₓ was not removed from flue gas before CO₂ adsorption in a special section [9]. According to these studies, a large part of the NOₓ was adsorbed—not in the desulfurization and NOₓ removal section, but in the CO₂ separation section, thus contaminating the activated carbon. The used activated carbon materials (in the four adsorption columns—CO₂ separation section) featured increased nitrogen content, which suggested the slight adsorption of NOₓ captured from the flue gas. Details of this analysis can be found in [9]. Many of the same results were obtained by Lee et al. [29] during a study on the surface of impregnated activated carbon after NOₓ and SO₂ adsorption. The authors observed that in most cases, adsorption proceeded during chemical reactions. Due to the presence of OH groups on the surface, the KOH-impregnated activated carbon oxidized due to NOₓ and SO₂ adsorption. In particular, SO₂ presented strong interactions with KOH-impregnated activated carbon, forming K₂SO₄ on the external surface of activated carbon. Lee et al. [29] also observed that more SO₂ adsorbed on the surface of KOH-impregnated activated carbon corresponded to less NOₓ being adsorbed. The authors in [29] showed that the individual adsorption of NOₓ and SO₂ proceeded differently than the simultaneous adsorption of both impurities. Many of the same conclusions were presented by Abdulrasheed et al. [27], who observed that the simultaneous removal of NOₓ and SO₂ using KOH-impregnated activated carbon in an environment rich in O₂ showed SO₂ to have higher affinity to the adsorbent than NOₓ. This was likely also the case in our research. On the other hand, when these gases were removed separately, NOₓ showed higher affinity than SO₂. The stronger affinity of SO₂ ensured a higher rate of chemisorption on the surface of impregnated activated carbon and the bonding of oxygen groups (needed for NO oxidation and further NO₂ adsorption on activated carbon), especially in the presence of moisture and sulfuric acid formation. The conducted research shows that the practical use of technology involving the simultaneous removal of both SO₂ and NOₓ still makes flue gas desulfurization and denitrification challenging and requires significant research in this area. This result was also confirmed by the study of Neathery et al. [30] on selective NOₓ capture from flue gas containing SO₂, CO₂, H₂O, O₂, and N₂. Neathery et al. observed that NOₓ can be selectively adsorbed from flue gas mixtures, but only under the proper conditions—i.e., a sufficiently high oxygen concentration, low SO₂ concentration, and a proper temperature range of 35–120 °C. This suggests that under our real research conditions on simultaneous SO₂ and NOₓ adsorption from flue gas, the above conditions were not met, leading NOₓ adsorption to be minimal. The conclusions of the study highlight that the simultaneous removal of both SO₂ and NOₓ from real CFB flue gas on impregnated activated carbon is still challenging and dependent on the particular conditions of the flue gas.

3.6. Analysis of Flue Gas Constitution before and after Leaving the Adsorber

Information obtained based on analysis of the physicochemical properties of AC-P before and after use in the deSO₂ and deNOₓ adsorber was also confirmed by analyzing the flue gas constitution before and after leaving the adsorber (marked as points 1 and 2 in Figure 2). Figure 9a shows that before entering the adsorber, almost all the SO₂ contained
in the flue gas was captured via impregnated AC-P, and the volume of SO₂ in flue gas leaving the adsorber did not exceed 5 mg/Nm³ (SO₂ content at the adsorber inlet was 1–111 mg/Nm³).

![Figure 9](image_url)

**Figure 9.** Online analysis of SO₂ concentration (a) and NOₓ concentration (b) in the flue gas before and after leaving the deSOₓ and deNOₓ adsorber (the temperature of the CFB flue gas was 25 °C, the maximum capacity of the DR-VPSA installation was 100 Nm³/h, the measuring campaign was 808 h).

This result confirmed the efficacy of desulfurization in the deSOₓ and deNOₓ adsorber. The total SOₓ removal efficiency amounted to 95.5–100%. Similar results were reported by Ishibashi et al. [4,5]. In [4,5], SO₂ removal was so effective that no SO₂ accumulation was observed in the CO₂ adsorbent removed after 2000 h of use in a PTSA/PSA adsorption installation for CO₂ capture. The authors also stated that for CO₂ capture VPSA processes, installing a SOₓ desulfurization and NOₓ removal section was less expensive than accepting the adsorbent degradation when the flue gas contained more than 10 mg/Nm³ SO₂ and 10 mg/Nm³ NOₓ [4,5]. Our analysis of the adsorbent also confirmed the effective removal of SO₂ in the pre-treatment section. Replacement of the AC-P sorbent that filled the deSOₓ/deNOₓ adsorber was not necessary after 808 h of DR-VPSA operation because no increase in the SO₂ concentration at the outlet of the column was observed. This result confirmed the effectiveness and lifespan of the adsorbent used to remove SO₂. However, the situation was different for nitrogen oxides, which were not captured in the adsorber, as shown in Figure 9b. The content of nitrogen oxides in the flue gas (reaching
55–120 mg/Nm\(^3\) before entering the adsorber) dropped by only a few mg/Nm\(^3\) after leaving the adsorber. However, it never exceeded 120 mg/Nm\(^3\). In a previous study completed by the same authors of the present work [9], uncaptured NO\(_x\) progressed to the CO\(_2\) separation section (DR-VPSA), where it was adsorbed on the CO\(_2\) adsorbent and as a result of cyclic sorption/desorption processes, mixed with recirculating gas and ultimately appeared as impurities in the final CO\(_2\) product [8]. This result confirmed that the process of removing NO\(_x\) in desulfurization and the NO\(_x\) removal section was ineffective.

4. Conclusions

The present results based on real CFB flue gas at the Lagisza Power Plant demonstrated that using AC impregnated with KOH and KJ in the adsorber to remove sulfur and nitrogen oxides in the pre-treatment module of the adsorption CO\(_2\) capture unit (DR-VPSA) was a solution that ensured sufficient flue gas purification and the removal of sulfur oxides. However, this method is insufficient for nitrogen oxides. The impregnated activated carbon showed adequate sorptive properties and proper thermal stability. It also did not change its properties during prolonged use in the adsorber. The tested activated carbon allowed for the effective removal of sulfur oxides under the continuous operation of the DR-VPSA installation for variable SO\(_2\) and NO\(_x\) loading in real flue gas conditions. This was confirmed by completed analyses of the spent activated carbon, which allowed finding the presence of SO\(_2\) adsorption products with chemical reaction, as potassium sulfate, on the surface of the spent activated carbon. From among the various alternatives, the removal of impurities from the flue gas through adsorption on surface-modified KOH/KJ activated carbon proved to be an efficient and reliable technology for sulfur oxides. However, the removal of nitrogen oxides under real conditions was not assessed.

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