Near-Zero Emissions Oxy-Combustion Flue Gas Purification

Task 3: SOx/NOx/Hg Removal for Low Sulfur Coal

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Abstract

The goal of this project was to develop a near-zero emissions flue gas purification technology for existing PC (pulverized coal) power plants that are retrofitted with oxy-combustion technology. The objective of Task 3 of this project was to evaluate an alternative method of SOx, NOx and Hg removal from flue gas produced by burning low sulfur coal in oxy-combustion power plants. The goal of the program was to conduct an experimental investigation and to develop a novel process for simultaneously removal of SOx and NOx from power plants that would operate on low sulfur coal without the need for wet-FGD & SCRs.

A novel purification process operating at high pressures and ambient temperatures was developed. Activated carbon's catalytic and adsorbent capabilities are used to oxidize the sulfur and nitrous oxides to SO_3 and NO_2 species, which are adsorbed on the activated carbon and removed from the gas phase. Activated carbon is regenerated by water wash followed by drying.

The development effort commenced with the screening of commercially available activated carbon materials for their capability to remove SO_2. A bench-unit operating in batch mode was constructed to conduct an experimental investigation of simultaneous SOx and NOx removal from a simulated oxyfuel flue gas mixture. Optimal operating conditions and the capacity of the activated carbon to remove the contaminants were identified. The process was able to achieve simultaneous SOx and NOx removal in a single step. The removal efficiencies were >99.9% for SOx and >98% for NOx. In the longevity tests performed on a batch unit, the retention capacity could be maintained at high level over 20 cycles. This process was able to effectively remove up to 4000 ppm SOx from the simulated feeds corresponding to oxyfuel flue gas from high sulfur coal plants.

A dual bed continuous unit with five times the capacity of the batch unit was constructed to test continuous operation and longevity. Full-automation was implemented to enable continuous operation (24/7) with minimum operator supervision. Continuous run was carried out for 40 days. Very high SOx (>99.9%) and NOx (98%) removal efficiencies were also achieved in a continuous unit. However, the retention capacity of carbon beds for SOx and NOx was decreased from ~20 hours to ~10 hours over a 40 day period of operation, which was in contrast to the results obtained in a batch unit. These contradictory results indicate the need for optimization of adsorption-regeneration cycle to maintain long term activity of activated carbon material at a higher level and thus minimize the capital cost of the system.

In summary, the activated carbon process exceeded performance targets for SOx and NOx removal efficiencies and it was found to be suitable for power plants burning both low and high sulfur coals. More efforts are needed to optimize the system performance.

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Executive Summary

The objectives of this project were to carry out an experimental program to 1) enable development and design of a near zero emissions oxy-combustion flue gas purification processes having a high CO_2 recovery for power plants burning high and low sulfur coals and, 2) to perform commercial viability assessment on the proposed technology.

The purpose of the Task 3 program was to investigate an alternative method of SOx and NOx removal from flue gas produced by burning low sulfur coal in oxy-coal power plants. In a typical power plant SOx is removed by reaction with lime or limestone producing disposable gypsum using a wet or dry-FGD at atmospheric pressure. The lime/limestone reagent cost, gypsum disposal cost, parasitic power plant load and equipment capital costs can be substantial. NOx removal is typically achieved in an SCR which requires ammonia as reagent, and substantial capital investment. Instead of processing flue gas at low pressures, the proposed Task 3 process aims to process flue gas at high pressure within the oxy-coal CO_2 processing unit (CPU).

The process developed relies on direct oxidation of both SO_2 and NO using activated carbon. In the presence of oxygen at ambient temperature, activated carbon acts as catalyst for the oxidation of SO_2 and NO. The oxidation products, SO_3 and NO_2, remain adsorbed on the carbon surface. When the flue gas stream containing oxygen and contaminants are passed over an activated carbon bed, the effluent essentially free of SOx and NOx is obtained. After carbon bed is saturated with SOx and NOx, it is regenerated by washing with water, followed by drying. Water reacts with the SO_3 and NO_2 to form dilute solution of sulfuric and nitric acids. A drying step is required to remove the water adsorbed on the active sites in order to complete the regeneration stage. A multi-bed system comprising of at least two beds is required for continuous operation with one bed on adsorption and other on regeneration.

Task 3 was composed of 5 subtasks. In an initial stage, subtask 3.1 focused on screening of commercially available catalytic carbon materials. Material samples were obtained from six suppliers and tested for their performance of removing SO_2 only from a simulated flue gas in a simplified experimental rig. A preferred activated carbon material was selected for further experimental investigation. Optimal design parameters for designing a bench-scale test unit were also defined in this stage.

The main activity of subtask 3.2 was to design and build a bench-scale unit with a capacity of ~0.025 tpd CO_2. In Subtask 3.3, influence of various process parameters such as pressure, temperature, and feed composition (water vapor; SO_2 and NO concentration) on process performance was investigated. A design of experiments approach was used. The results showed excellent simultaneous removal of SOx and NOx, with efficiency higher than 99.9 % for SOx and up to 98 % for NOx exceeding the program targets of 99% and 95%, respectively. The CO_2 purification and the activated carbon material capacity to simultaneously retain SOx and NOx are favorably influenced by lower temperatures (ambient), and higher pressures. It was shown that the presence of NO

enhances SO_2 removal. Water presence in the vapor phase has an interesting effect. It enhances SOx removal, most probably due to formation of H_2SO_4 on the surface of the activated carbon, but it has a disadvantageous effect on NOx retention. It was observed that as long as the water vapor concentration stays below the SOx concentration in the feed, the water is consumed and contributes to augment the process performance. Any excess water vapor negatively affects the NOx removal and reduces the retention capacity of the activated carbon for the contaminants.

Subtask 3.4 consisted of a paper study on commercial methods for mercury removal. Due to the nature of the process, mercury condenses in various stages of the CO_2 purification, more specifically in the condensate obtained in the flue gas compression train. Due to the acidic nature of the waste water obtained during the regeneration stage of the activated carbon process, part of mercury is expected to dissolve in the waste water.

A new Subtask 3.5 was added in the project scope in the final year of the project due to encouraging results obtained earlier. This Subtask focused on testing the activated carbon process in a scaled-up two-bed continuous unit. The process was scaled up by 5X to ~0.125 tpd CO_2 equivalent capacity. The continuous unit consisted of two fixed bed reactors with valve skid to ensure continuous feeding of simulated flue gas. Full automation was used to enable continuous operation with minimum operator supervision, in order to test the activated carbon longevity and its performance evolution with operating time. It was observed that during the course of 40 days of continuous testing (24/7) the breakthrough time gradually dropped down from ~20hrs to ~10hrs. The drop was steep till 12th cycle after which it was more gradual. However, the SO_2 and NO removal efficiencies of ~100% and 97-98% were maintained during the whole testing period. Reduction in the breakthrough time suggests that improvement on regeneration stage is needed.

As proposed, the potential advantages of the Task 3 process was the ability to simultaneously remove SOx and NOx impurities, with high efficiency, and eliminate or reduce the need for traditional flue gas purification technologies (FGD and SCR). The following major conclusions can be made: 1) Commercially available activated carbon materials are suitable for simultaneously SOx and NOx removal at elevated pressures and ambient temperatures; 2) Continuity and scalability of the process is achievable through a multi-bed reactor design and a sequential operating schedule; 3) Good purification performance can be achieved, more specifically the contaminant content in the stream exiting the purification stage is: SOx <10 ppm, NOx <20 ppm.

Approach

Task 3 was composed of 5 subtasks. In an initial stage, Task 3.1 focused on screening of commercially available catalytic carbon materials for their performance to remove SO_2 from concentrated CO_2 stream. A bench-unit was designed and built as scope of subtask T3.2. A comprehensive experimental investigation was carried out under subtask T3.3. A paper study for mercury removal was completed as part of subtask T3.4. The aim of subtask 3.5 followed the successful demonstration of excellent simultaneous SOx and NOx removal in previous tasks, and had as main objective designing, building, and operation of a dual bed continuous unit. The latter was used to assess the activated carbon longevity and its performance change over time.

The following paragraphs provide the detailed approach used for each subtasks. In addition, technology, process and chemistry are described as background information.

Technology Description

The purpose of Task 3 project was to investigate an alternative method of SOx and NOx removal from flue gas produced by burning low sulfur coal in oxy-coal power plants. The process applies to oxy-combustion flue gas which is to be further compressed and processed for CO_2 capture and sequestration (CCS). Figure 1 shows a high level diagram of an oxy-combustion boiler for this application where two streams of recirculated flue gas are used to moderate boiler temperature. This Figure shows the primary 'air' being treated in an FGD due to material of construction issues in the coal pulverizing and conveying equipment. Secondary air is not required to be treated. Combustion energy is used to generate steam and a turbine is used for power generation. The flue gas produced from the boiler island is then treated in the CO_2 processing unit (CPU) for CO_2 compression and purification.
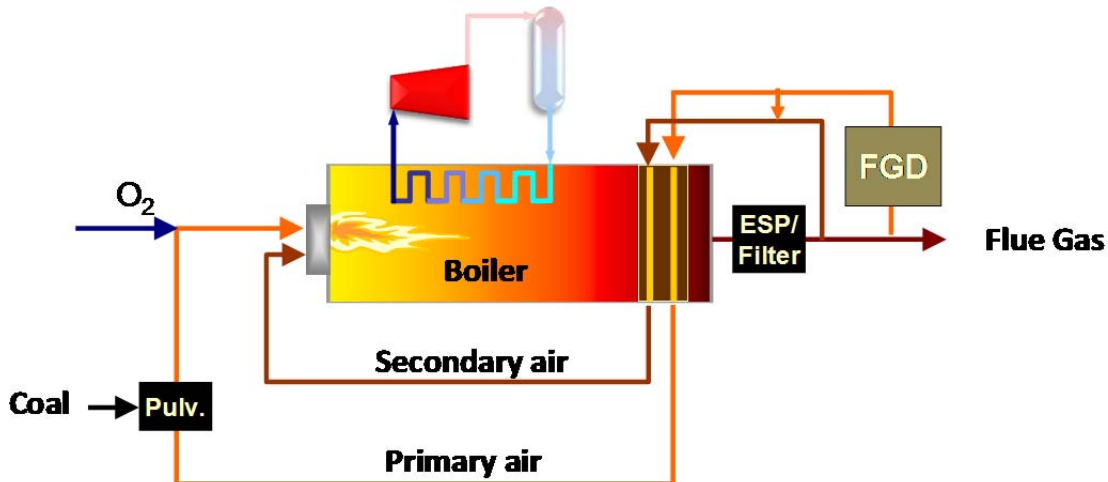

Figure 1. Schematic of the Oxy-coal Boiler Island

In a typical power plant SOx is removed by reaction with lime or limestone, producing disposable gypsum using a wet or dry-FGD at atmospheric pressure. The lime/limestone

reagent cost, gypsum disposal cost, parasitic power plant load and equipment capital costs can be substantial. NOx removal is typically achieved in an SCR which requires substantial capital investment and also requires ammonia reagent.

The goal of this project was to develop a process, which simultaneously removes SOx and NOx within an oxy-coal CPU. Figure 2 shows a high level diagram of the entire CPU process. Raw flue gas from boiler is cooled and then compressed. Next the flue gas is treated in the proposed Task 3 process for SOx and NOx removal. Following the Task 3 process the flue gas is purified in a Cold Box cycle to concentrate the CO_2. The purified CO_2 is further compressed to the final product pressure. The 'Cold Box Vent' stream is processed in a vacuum pressure swing adsorption (VPSA) process to recover CO_2 which is recycled to the raw gas compressor. The process vent gas, mostly composed of O_2, N_2 and Ar is heated and expanded for power recovery.
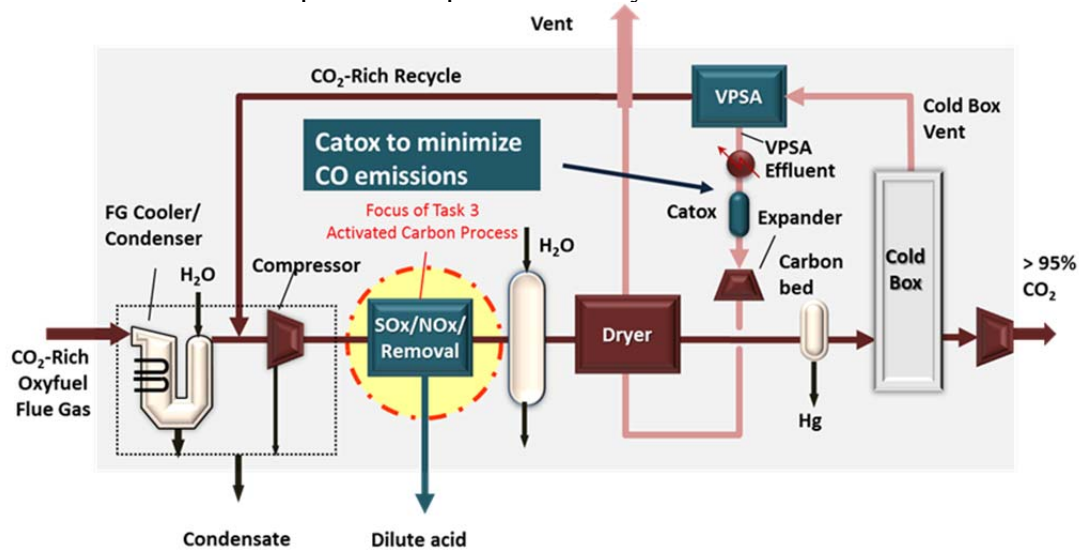

Figure 2. A CPU with Activated Carbon Process for SOx/NOx Removal

Process Description

Figure 3 below shows the configuration of the Task 3 process for flue gas purification by simultaneously removing SOx and NOx at high pressure. In order to ensure continuous operation, the process must consist of at least two activated carbon beds alternatively operated in adsorption and regeneration modes. Typically the flue gas containing SOx and NOx passes through the carbon bed from bottom to top. Once the carbon bed in service is almost saturated with contaminants a valve system switches the flue gas feed to the second bed, while regeneration starts for the saturated bed. Regeneration of the carbon material is achieved by passing a stream of water from top to bottom. The waste water can be recycled in order to minimize the waste water generated. A drying step is required to remove the water adsorbed on the active sites in order to complete the regeneration stage. The nitrogen can be used for drying. The Task 3- treated flue gas would be further processed in the CPU to produce purified CO_2 stream.
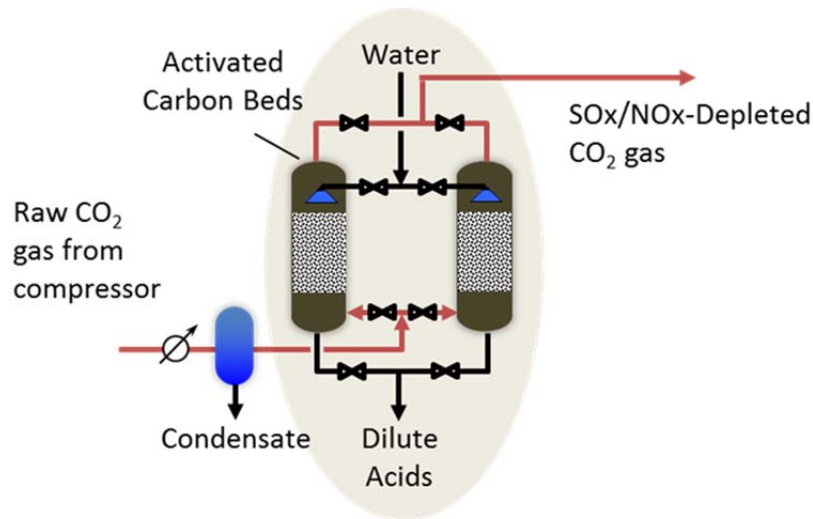
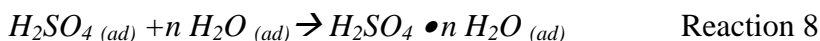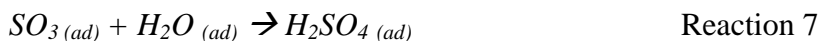**Figure 3. Task 3 Activated Carbon Process for SOx/NOx Removal**

Chemistry Description

In the Task 3 process a number of heterogeneous and homogeneous reactions take place for NOx and SOx oxidation, and formation of the sulfuric and nitric acids. The elevated pressure which would be present in the CPU is another key feature which increases the rates of adsorption related reactions and mass transfer fluxes.

Adsorption stage involves homogeneous and catalytic oxidation of the contaminants and adsorption of the oxidation products on the activated carbon material. The inferior oxides of sulfur and nitrogen are oxidized to their superior oxides by oxygen through the flowing reactions:

$NO + 0.5\,O_2 \rightarrow NO_2$ Reaction 1

$SO_2 + 0.5\,O_2 \rightarrow SO_3$ Reaction 2

Reaction 1 takes place homogeneously in the gas phase and is enhanced by high pressure and low temperature. Reaction 2 is heterogeneously catalyzed by the activated carbon. NO_2 and SO_3 are the species that are adsorbed on the carbon. Water presence in the vapor phase significantly affects the reaction mechanism for SO_2 removal. One of the proposed mechanisms [1] for SO_2 adsorption onto activated carbon in the presence of oxygen and water vapor is given below:

$SO_2 \rightarrow SO_{2\,(ad)}$ Reaction 3

$H_2O \rightarrow H_2O_{(ad)}$ Reaction 4

$0.5\ O_2 \rightarrow O_{(ad)}$ Reaction 5

$SO_{2\ (ad)} + O_{(ad)} \rightarrow SO_{3\ (ad)}$ Reaction 6

$SO_{3\ (ad)} + H_2O_{(ad)} \rightarrow H_2SO_{4\ (ad)}$ Reaction 7

$H_2SO_{4\ (ad)} + n\ H_2O_{(ad)} \rightarrow H_2SO_4 \bullet n\ H_2O_{(ad)}$ Reaction 8
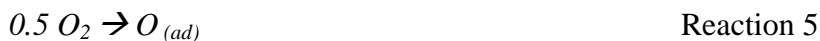
This mechanism suggests that once the H_2SO_4 is produced the active sites occupied by water and sulfur trioxide are freed and the activated carbon retention capacity increases. In addition the hydroscopic nature of the sulfuric acid makes possible to fix the water molecules from the gas stream. NO_2 can react with SO_2 in homogeneous phase and can act as a catalyst for oxidation of SO_2.

$SO_2 + NO_2 \rightarrow SO_3 + NO$ Reaction 9

Reaction 9 indicates that the presence of NO_2 enhances the oxidation of SO_2. If O_2 is present in excess, the NO formed in Reaction 9 can be easily re-oxidized.

Once the activated carbon is saturated, the SOx and NOx components breakthrough and their presence in reactor gas effluent can be detected. The adsorption capacity of the activated carbon can be restored by passing a water stream over the carbon bed. In this manner water reacts with SO_3 and NO_2 forming the corresponding acids.

$SO_3 + H_2O \rightarrow H_2SO_4$ Reaction 10

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$ Reaction 11

The regeneration stage consists of washing the activated carbon bed with water followed by drying with an inert gas stream (i.e. N_2 or CO_2). Consequently, most of the sulfur oxides can be captured as sulfuric acid. However, due to the stoichiometry of Reaction 11, a third of the NOx adsorbed on the activated carbon are produced back as NO during the regeneration stage.

Subtask 3.1 – SOx and NOx Removal Material Selection

The subtask 3.1 addressed selection of adequate activated carbon materials. Material selection was based on testing commercially available materials for SO_2 removal. Since SO_2 is typically the contaminant with a higher concentration, performance of its removal was considered as a first requirement for a preliminary material performance screening.

The PI&D of the experimental set-up for material screening is given in Figure 4. Each material was loaded as a fixed bed in a ¾" tube with a length of 12". A flow of process gas of 3 SLPM was passed over the fixed bed, ensuring at least 6s residence time. The process gas source was obtained by blending a mixture of 2% SO_2, 40 % O_2 in CO_2 from

a gas cylinder, with pure CO_2 delivered directly from a service tank. The typical composition of the process gas fed to the activated carbon bed was about 2000 ppm SO_2, 4% O_2 in CO_2. For tests to be performed at 80 C (176 F), the ¾" tube was placed in a furnace, which was controlled based on the temperature measurement taken by a thermocouple inserted axially in the middle of the bed. The process gas pressure was maintained at about 15 bar (221 psia).
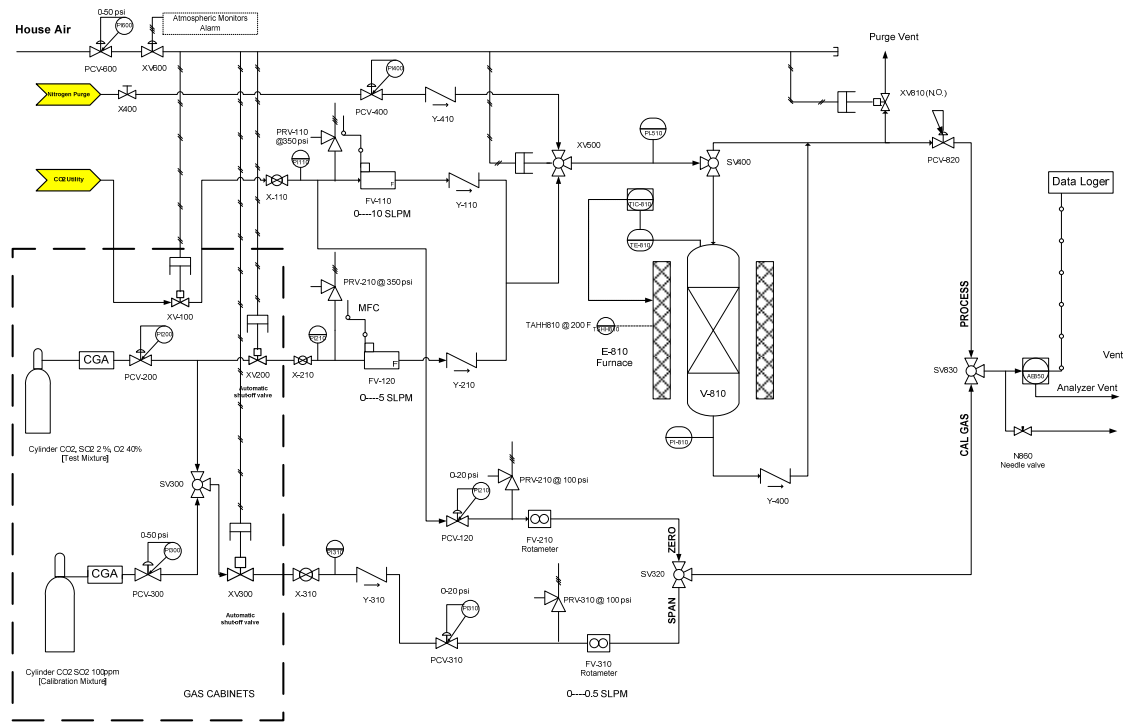
Figure 4. PI&D of the Experimental Set-up for Material Testing.

The test procedure consisted of three consecutive steps. First, a break-through test for SO_2 was carried out by passing the process gas containing SO_2 over the activated carbon bed. The SO_2 concentration was monitored continuously by means of a PG250 Horiba Analyzer. The test was completed when the SO_2 concentration in the effluent stream reaches 100 ppm. In the second step, the bed saturated with SO_2 was regenerated by water washing. In the last step, a small amount of inert gas, more specifically N_2, was passed through the bed to remove free water. The materials were tested for at least three consecutive cycles. The performance index utilized to compare various activated carbon materials was calculated as the amount of SO_2 removed per unit weight of carbon in the bed. Six different materials were tested. The material that had the capacity to retain the highest amount of SO_2 was selected for further testing of simultaneous removal of SOx and NOx.

## Subtask 3.2 – Design and Construction of the Bench Unit

The scope of this subtask was to build a bench-scale unit operated in batch mode for a comprehensive experimental investigation of simultaneously SOx and NOx removal over a wide range of operating conditions and feed compositions. The PI&D of the bench-unit is given in Figure 5. A fixed bed test reactor containing about 100 g of activated carbon, and a simulated flue gas flow of 10 SLPM were used. The test reactor had a diameter of 1", while the length of the carbon bed was about 18". The simulated gas flow mixtures flows from top to bottom. A high precision high pressure water pump was used to provide the amount of process water so that the feed composition achieved up to 1800 ppm of water vapors. On top of the activated carbon bed, 6" height of inert ceramic beads were used to ensure mixing of the process gas with process water, and water vaporization.

Typical flue gas composition used during the investigation was:

85-90 % (vol.) CO_2
4-6 % (vol.) N_2
2-6 % (vol.) O_2
200-750 ppmv NO
1000-3000 ppmv SO_2

The source of SO_2 component was provided by gas cylinders of 6 % SO_2 in N_2, while the source for NO component was provided from 3% NO in N_2 gas cylinders. High purity O_2 gas cylinders were used to deliver the required O_2, while pure CO_2 was delivered directly from a service tank. Mixtures with various compositions and humidity levels were prepared by adjusting the mass flow controllers used to deliver each gas stream and the high precision high pressure water metering pump for water delivery.

In order to maintain the test bed at constant temperature, up to 80 C (176 F), the 1" test reactor was placed in a heating blanket, which was controlled based on the temperature measurement taken by a thermocouple inserted axially in the middle of the activated carbon bed. The process gas pressure of up to 15 bar (221 psia) was maintained by means of a back-pressure regulator. The experimental-set up was provided with capabilities for regeneration by washing it with water, and drying with nitrogen.
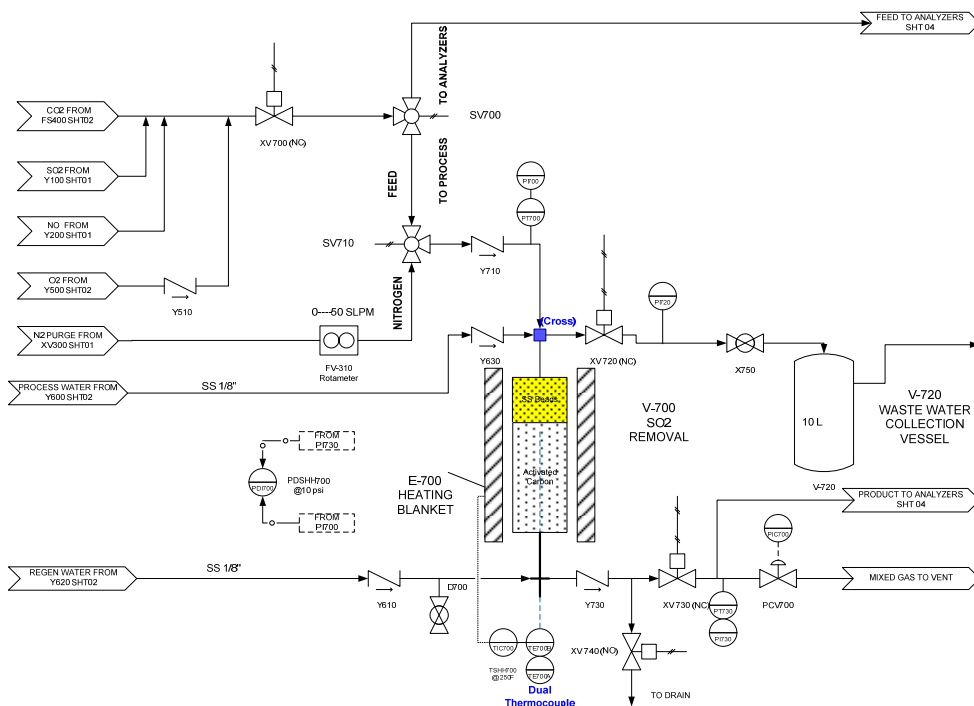
Figure 5. P&ID of the Bench Unit for Simultaneous SOx/NOx Removal

The SO_2, NO, and NO_2 concentrations of the gas stream exiting the test reactor were monitored continuously by the Emerson Analyzer. A sample conditioning system based on Nafion membrane was utilized to remove the water contained in the process gas stream before sending it to the analyzers.

A fairly high degree of automation was included to comply with safety requirements, to allow remote control, and acquire relevant experimental data. For this purpose a Programmable Logic Controller (PLC) and a user interface design in LabView was used. Due to high toxicity of the gaseous components involved, precautions were taken to ensure safety measures and protection of operators. The feed and calibration gases containing SO_2 and NO were placed in a secured gas cabinet provided with appropriate vents. Continuous atmospheric monitors for the toxic components were installed. Any detection of the toxic gases initiated the automatic shut-down of the system. Automatic shut-off valves, for the feed gases and water used for process and regeneration, were provided in the system for this purpose. In case of emergency shut-down, a flow of nitrogen purged the entire system.

The bed was regenerated by flowing water from bottom to top such that the total volume of regeneration water flown was at least 6 times the carbon volume. The waste water was collected in a vessel, neutralized with sodium bicarbonate and discharged. Waste water samples were collected for selected experiments and analyzed for their content of the

following ions: *Sulfates (SO$_4^2$), Nitrates (NO$_3^-$), Nitrite (NO$_2^-$)*. A Hach 890 colorimeter was used for this purpose.

Subtask 3.3 – SOx/NOx Removal Tests

An experimental plan was designed to investigate the influence of several key operating parameters on process efficiency and carbon capacity to retain the SOx and NOx. The investigated operating parameters were: temperature, pressure, inlet composition (NO / SO$_2$ molar ratio), presence of water in the inlet flue gas stream, and total inlet flowrate (residence time). A two-level factorial design was employed to screen the impact of key process variables for simultaneous removal of SOx and NOx on activated carbon. The values for the high-low levels considered for each parameter are given in Table 1.

Table 1. Ranges for the Two Level Factorial Design for Selected Parameters

Parameter	Low	High
Temperature, C	20	80
Pressure, bar	3.4	15
Feed Humidification	No (Dry)	Yes (Saturation)
Total Feed Gas Flow, SLPM	10	25
SO$_2$ Concentration, ppm	2000	4000
NO Concentration, ppm	0	750

A total of 24 carbon beds were tested for selected conditions. For each bed the adsorption-regeneration cycle was repeated 3-5 times. During each breakthrough test the reactor gas effluent composition was continuously monitored. The breakthrough completion was considered at the time when either contaminant (SOx or NOx) achieved 30 ppm in the reactor gas effluent. For the adsorption stage, the process performance was determined by calculating the amounts of contaminants retained on the activated carbon, as well as the efficiency of their removal from the gas stream. The retention of each contaminant is calculated as:

$$\text{Retention}_i = \frac{\left[\int_0^{BT} \left(F_i \cdot y_i^{in} \right) dt - \int_0^{BT} \left(F_T \cdot y_i^{out} \right) dt \right] \cdot \frac{1}{V_0}}{m_{carbon}}, \frac{m\text{oles of SO}_2 \text{ or NO}}{\text{g Carbon}} \quad (1)$$

Where:
i   NO, or SO$_2$
F$_i$ gas flow of fed contaminant from source, SLPM
y$^{in}_i$ molar fraction of contaminant i from source
F$_T$ total gas flow rate at the reactor outlet, SLPM
y$^{out}_i$ molar fraction of contaminant i at reactor outlet
t   time, min
BT   breakthrough time (to 30 ppm of SO$_2$ or NO), min

V_0 molar volume in standard conditions, l/mole

A cumulative molar retention can be calculated as:

$$Retention_{SO_2 + NO} = Retention_{SO_2} + Retention_{NO} \qquad (2)$$

The removal efficiency for each component is calculated as

$$Efficiency_i = \frac{\left[\int_0^{BT} \left(F_i \cdot y_i^{in} \right) dt - \int_0^{BT} \left(F_T \cdot y_i^{out} \right) dt \right] \cdot}{\int_0^{BT} \left(F_i \cdot y_i^{in} \right) dt} \cdot 100 \qquad (3)$$

Subtask 3.4 – Mercury and Residual NOx Removal Research

In any conventional coal fired power plant, mercury emission is an environmental issue, wherein current regulations in several countries require its removal down to less than 5-10 mg/MWh. However, in any oxy-coal combustion power plant with CO_2 capture, mercury is not only an environmental issue but also an operational issue specifically to any aluminum based heat exchangers (BAHX) used in the CO_2 clean-up and processing unit. It may be expected that mercury should be removed down to 0.01 μg/Nm^3 (this is the current standard applied in any NG/LNG plant) [2]. A literature survey was conducted to assess the current state of art for mercury removal options.

Subtask 3.5 – Continuous Operation Unit

A continuous unit was designed and built to address the scalability of the process, to prove continuous operation 24 h x 7 days per week, and to test the activated carbon material longevity.

The system was designed to fit in a walk-in hood. It was assembled on three removable skids: *gases and water supply skid*, *reactor skid*, and *analytical skid*. This modularity ensured easy access for maintenance and potential modifications. The supply skid contained the mass flow controllers for the source gases, the water pumps for process water and regeneration water, and a high pressure high precision pump for liquid SO_2 delivery. The gas supply system delivered CO_2, specialty gases and N_2. The CO_2 was delivered from a six-ton bulk tank located outside the building. SO_2 source was either a 6 % SO_2 in N_2 mixture delivered from a gas cylinders or liquid SO_2. NO source was a 3 % NO in N_2 mixture delivered from a gas cylinder. The cylinders of toxic gases were placed in gas cabinets adjacent to the hood.

The P&ID of the reactor skid is given in Figure 6. It consisted of two fixed bed reactors holding activated carbon. Each bed had a diameter of 2" and a length of 20". To ensure

good flow distribution a segment of inert packing was placed above and below the carbon bed. The flue gas containing SOx and NOx passed through the carbon bed from bottom to top. Once the carbon bed in service was saturated with contaminants, a valve system switched the flue gas feed to the second bed; and regeneration started for the saturated bed. Regeneration of the carbon material was achieved by flooding the carbon beds with water from bottom to top. A pair of electronic level indicators was used to show the water level in the reactor vessel and signal when the water covered the height of the carbon bed. Once flooded, the reactor held the water for 10 min, and then the water was drained at the bottom of the bed by slightly pressurizing the reactor with nitrogen. This flooding sequence was repeated at least 6 times to ensure removal of the sulfuric and nitric acid formed during the regeneration stage. After washing with water, the carbon bed was dried using nitrogen at 180 ^{o}F. The dried bed was cooled by passing nitrogen at ambient temperature.

The simulated flue gas contained 450 ppm SO_2, 200 ppm NO, 4 % O_2, 94 % CO_2, water vapor of about 1725 ppm (saturation level), and N_2 as balance. The gas flow was delivered at 250 psia and ambient temperature. The unit was designed for continuous operation. For this purpose full automation was implemented to meet safety standards and allow it to run unattended. The reactor outlet gas composition was continuously monitored using an MLT Rosemount/Emerson analyzer. During the regeneration stage, potential gases degassing from the carbon beds were redirected towards a second analyzer (Horiba PG-250) by using a secondary flow of carbon dioxide. This was done to quantify the amount of contaminants that were not captured in the liquid phase during the regeneration stage.

Adsorption/regeneration cycles were carried out 24/7 for 40 days. The waste water was neutralized before discharging. Occasionally, the waste water was sampled and its content of SO_4^{2-}, SO_3^{2-}, NO_3^-, and $NO2^-$ was analyzed in order to determine the amount of SOx and NOx converted to sulfuric and nitric acid. Standard colorimetric methods for waste water analysis were used.
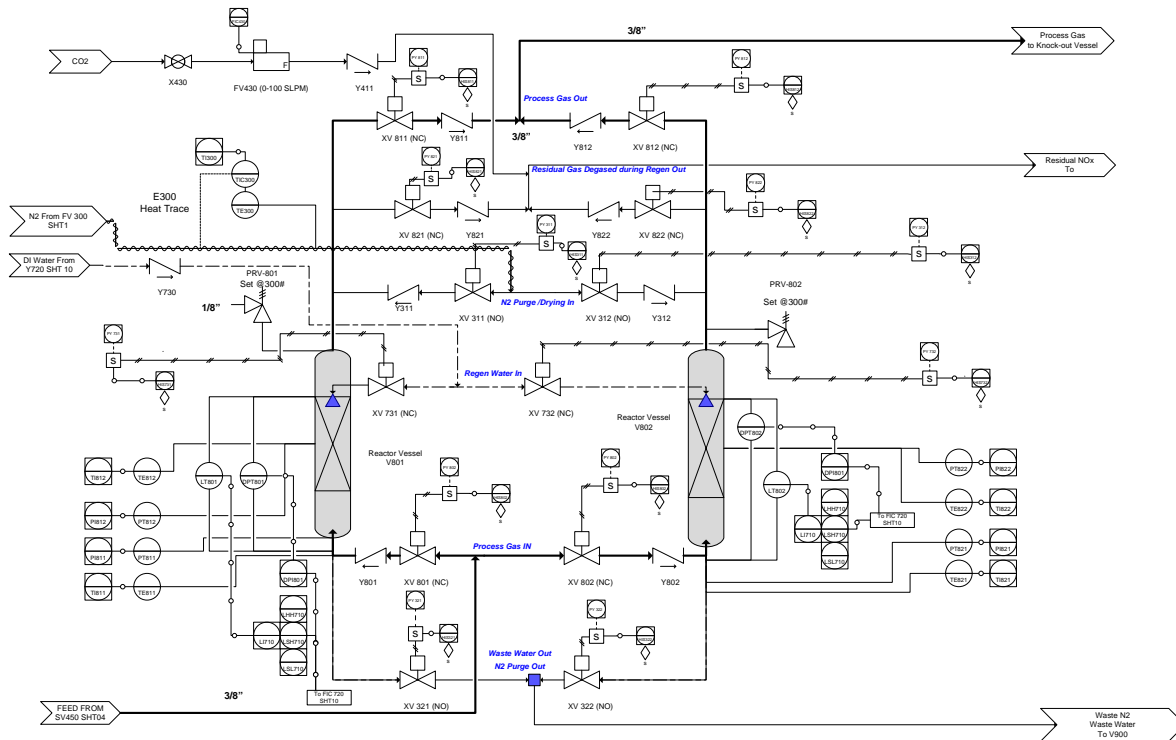
Figure 6. Dual Bed Reactor System for Simultaneous SOx/NOx Removal

The main goal of the experimental investigation is to understand how the carbon material capability to simultaneously remove traces of SOx and NOx evolve during a period of two months of continuous operation. The workflow for the proposed experimental program is given in Figure 7.
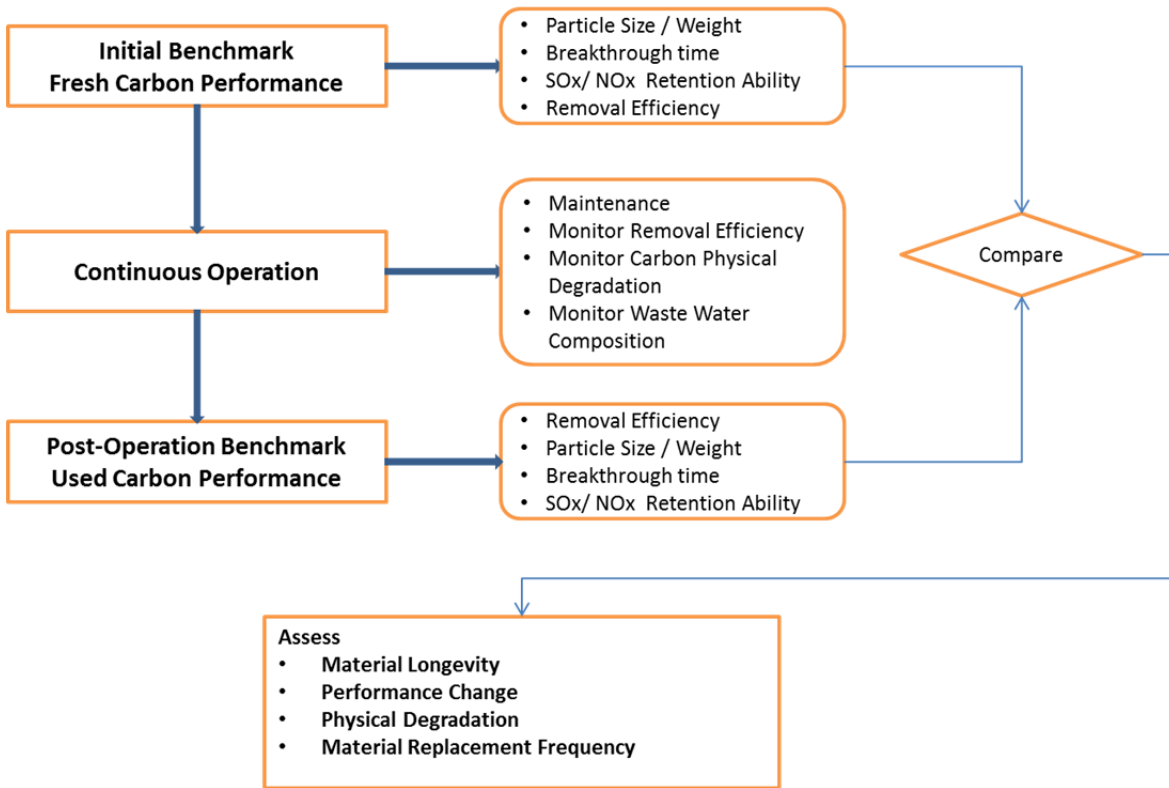
Figure 7. Workflow to Assess the Activated Carbon Material Longevity

First a benchmark is established for the fresh carbon. More specifically, the breakthrough time and consequently the initial amount of SO_2 and NO retained per unit mass of activated carbon, was determined for a set of inlet conditions for both beds. For the benchmarking purpose, the adsorption stage was conducted till breakthrough of any of the contaminants occurred. In this particular study, the breakthrough time is considered to take place when any of the contaminants: SO_2 or NOx concentration reaches 30 ppm in the gas stream leaving the reactor skid.

After the benchmarking was defined, the unit operated almost continuously for 40 days. The advanced automation and safety features allowed the unit to run 24 h/day with minimum supervision and unattended during weekends. The outlet concentration of all components was monitored continuously. It was sought to understand primarily if continuous operation altered the carbon material performance.

In order to ensure the process continuity, two parallel beds were used. While one bed operated in adsorption mode, the second bed was regenerated. A generic operating schedule is given in Table 2.

Table 2. Dual Bed Activated Carbon Unit Cycle Steps

Cycle	1			2		
Bed A	Adsorption			Washing	Drying	Hold
Bed B	Washing	Drying	Hold	Adsorption		

Continuous operation was configured so that the adsorption stage duration was at least equal or higher than the duration of the regeneration (washing and drying of the other carbon bed). A continuous and smooth transition from the bed in service to the regenerated bed was achieved.

At the end of continuous operation period, a similar systematic evaluation of the breakthrough time, and SOx/NOx removal efficiency and capacity was reassessed. The results were compared with the initial benchmarking in order to conclude how the activated carbon material changed its capability to simultaneously remove SOx and NOx.

Results and Discussion

Subtask 3.1 – SOx and NOx Removal Material Selection

Six samples of commercially available activated carbon were tested. Figure 8 compares the SO_2 removal performance of these samples. The SO_2 retention is calculated using equation (1) and then is scaled based to the best performance among all experiments. Figure 8 gives a comparison on relative bases for all samples investigated, and each cycle.

For the first cycle, the sample was loaded as received from the suppliers, while the following cycles are performed after the materials had undergone regeneration by water washing. No extensive drying was applied; therefore the moisture content in the bed in subsequent cycles was significantly higher as compared to the first cycle. This explains lower SO_2 retention by the carbon bed in the first cycle as compared to the following 2 cycles.
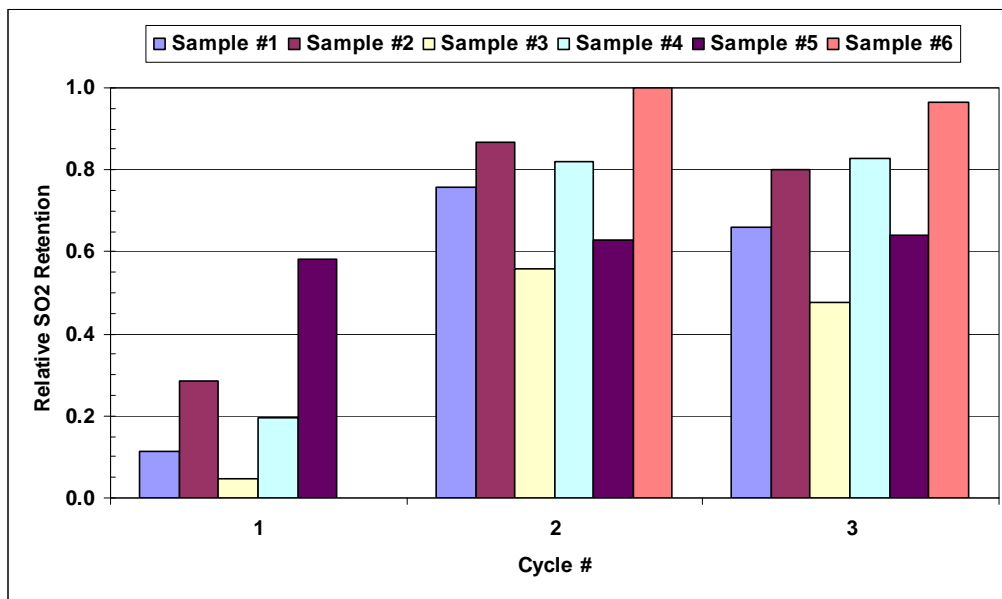
Figure 8. Relative Retention of SO_2 for Different Activated Carbon Samples

The relative SO_2 retention on the tested samples ranged from 0.55 – 1 (excluding cycle 1 results). Considering the variations in test conditions, measurement errors and limited number of tests, the performance of these samples are considered comparable. Material represented by Sample #2 was selected for simultaneous SOx and NOx removal in the bench unit designed and assembled as part of subtask 3.2.

Subtask 3.2 – Design and Construction of the Bench Unit

The bench unit for simultaneously SOx and NOx removal is shown in Figure 9. It had a compact lay-out to fit all the components in a designated hood. Easy access to all manual valves and instrumentation was available in order to maintain safe and efficient

operation. The gas cabinets containing the cylinders with toxic gases for process investigation and calibration are shown in Figure 10. Also, Figure 10 shows on the right hand side the PLC box.
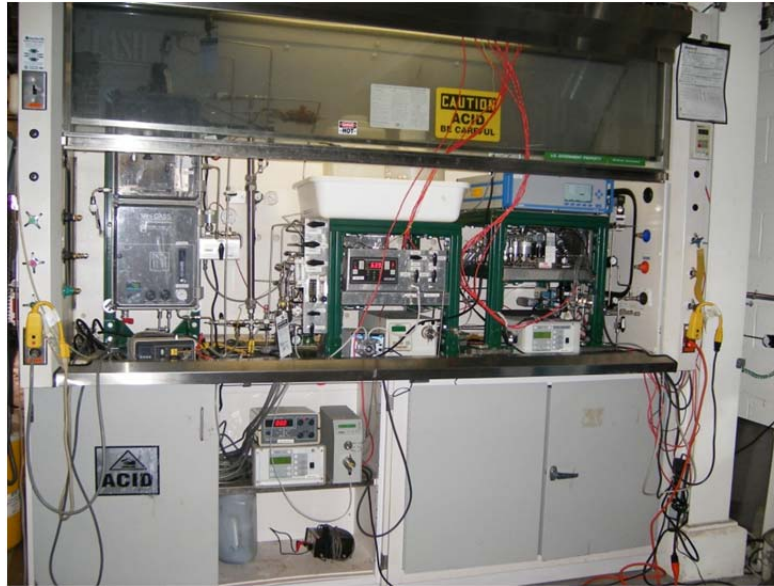

Figure 9. Bench Unit for Batch Mode Operation

Figure 10. Gas Cabinet for Toxic Gas Cylinders Storage and PLC Box.

One of the challenges encountered during operation of the experimental set-up was related to the humidification of the feed stream. The initial solution was to inject a small amount of water to the main gas stream before entering the reactor. It was observed that the process water delivery and its vaporization prior to entering the reactor bed did not provide a constant flow and composition in the feed stream of the water vapors. To avoid

this shortcoming, the system was modified to include a humidifier vessel. This enabled the CO_2 stream to pass through a column of water and to saturate with water vapors. The humidifier vessel concept is shown in Figure 11. The vessel consists of pipe with 4" diameter and 3' height, and contains 0.5 l water. The CO_2 stream with flows in the range of 10-25 SLPM is fed through a ¼" pipe and directed towards the bottom of the vessel. A sparger delivers the gas flow across the vessel cross-section. Steel wool is used as packing to ensure enhanced gas-liquid interfacial area. In this manner the gas bubbles through the liquid water from bottom to top, leaving the vessel close to saturation conditions. A baffle was provided to minimize the possibility of carrying liquid water along with the gas stream.
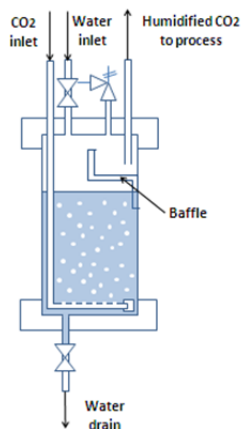
Figure 11. Schematic of CO_2 humidifier

The water content in the CO_2 stream was confirmed by performing humidity measurements using a Moisture Monitor Series 35 from Panametrics. The measurements showed good correlation with the theoretical saturation levels. This design was used for a more in-depth investigation of the water content impact on the process performance.

Subtask 3.3 – SOx/NOx Removal Tests

The results of a typical breakthrough test are shown in Figure 12 as time dependence of measured reactor outlet concentration for SO_2 and NO. Usually the NO breaks through first and exhibits a gradual increase of outlet concentration as compared with SO_2 which shows a sharper breakthrough. These breakthrough curves were used to calculate the retention and contaminants removal efficiency using the equations (1) – (3).

Dry feed containing 750 ppm NO, 2000 ppm SO$_2$, and 4 % O$_2$
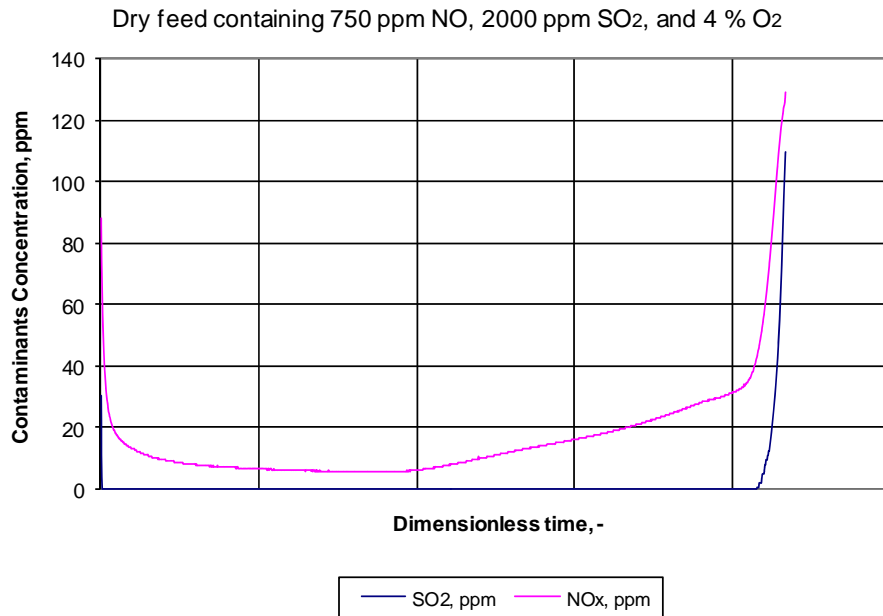
Figure 12. Reactor Outlet SO$_2$ and NOx Concentrations as a Function of Time

The experimental results for each bed reported on relative bases are given in Table 3. The retention values reported in Table 3 are scaled using the bed number 9 as benchmark. The molar retention considered is an average for the number of adsorption-regeneration cycles completed for each bed. In Table 3, columns I and J contain individual relative retentions of NO and SO$_2$ respectively, while column K shows the combined relative retention. Columns L and M display the removal efficiency as calculated by equation (14). Overall the results obtained indicate a good simultaneous removal of SOx and NOx with efficiency higher than 99% for SO$_2$ and 93% for NOx. The influence of the operating conditions investigated is discussed below.

Table 3. Activated Carbon Process – Bench Unit Results

Bed Index	Total Flow	Inlet Composition			H$_2$O in Feed	Temp	Press.	Relative Retention (Benchmark Bed 9)			Efficiency	
		SO2, ppm	NO, ppm	O2, %				NO	SO$_2$	NO+SO$_2$	NO, %	SO2, %
	SLPM					C	psig					
A	B	C	D	E	F	G	H	I	J	K	L	M
1	10	0	750	0	No	20	220	0.0	NA	0.0	0.00	NA
2	10	0	750	4	No	20	220	1.7	NA	0.4	99.30	NA
3	10	2000	750	4	No	20	220	1.0	0.9	0.9	97.33	99.99
4	10	0	750	6	No	20	220	2.0	NA	0.5	97.20	NA
5	10	2000	750	4	No	80	220	0.6	0.6	0.6	97.30	99.99
6	10	0	750	6	No	80	220	1.1	NA	0.3	99.33	NA
7	10	2000	0	4	No	20	220	NA	0.6	0.4	NA	99.99
8	10	2000	750	4	Yes	20	220	1.6	1.6	1.6	97.30	99.99
9	10	2000	750	4	No	20	220	1.0	1.0	1.0	97.50	99.99
10	10	2000	0	4	Yes	20	220	NA	1.3	0.9	NA	99.99
11	10	2000	0	4	Yes	20	220	NA	1.3	1.0	NA	99.99
12	10	2000	750	4	No	20	220	1.0	0.9	0.9	99.80	99.99
13	10	2000	0	4	No	20	220	NA	0.4	0.3	NA	99.99
14	10	2000	750	4	Yes	20	220	1.0	1.0	1.0	97.60	99.99
15	10	2000	750	4	Yes	20	220	1.8	1.8	1.8	98.05	99.98
16	25	2000	750	4	Yes	20	220	1.0	1.0	1.0	96.95	99.97
17	10	2000	750	4	Yes	20	50	0.3	0.3	0.3	93.04	99.97
18	10	4000	210	4	Yes	20	220	0.1	0.9	0.7	93.90	99.99
19	10	4000	510	4	Yes	20	220	0.4	1.1	0.9	96.94	99.98
20	18	2000	750	4	Yes	20	220	0.9	0.9	0.9	94.72	99.97
21	10	2000	750	4	Yes	20	150	0.7	0.8	0.8	97.45	99.98
22	10	3000	510	4	Yes	20	220	0.4	0.9	0.8	97.55	99.98
23	10	2000	750	4	Yes	20	100	0.6	0.6	0.6	96.70	99.97

Influence of Temperature

Experiments were conducted at two different temperatures 80 ^{o}C and 20 ^{o}C respectively. It was observed that the activated carbon capacity to adsorb SOx and/ or NOx is almost doubled at ambient temperature than at 80 ^{o}C (see Figure 13). The removal efficiencies were higher than 97 % for NOx and higher than 99 % for SOx for both temperatures.
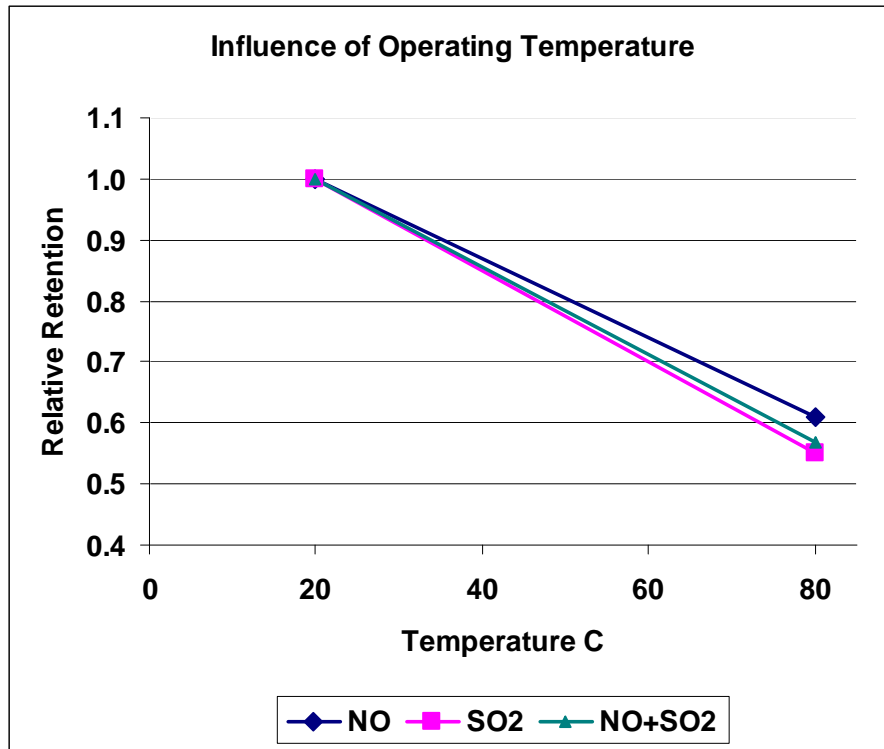
Figure 13. Influence of Temperature on Relative Retention of SOx and NOx

Influence of Pressure

Experiments were conducted at four different pressures 50, 100, 150, and 220 psig respectively. The activated carbon capacity to adsorb SOx and NOx significantly decreases with the decrease of pressure (see Figure 14). The SO_2 removal efficiency is less impacted by the decrease in pressure. Removal efficiency higher than 99 % is obtained for all pressures. The NO removal efficiency on the other hand is somehow more visible influenced by the decrease in pressure (see Figure 15). The NO removal efficiency is about 93 % at 50 psig and it increases to 97.3 % at 220 psig. This is a consequence of pressure influence on Reaction 1.

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Influence of Operating Pressure
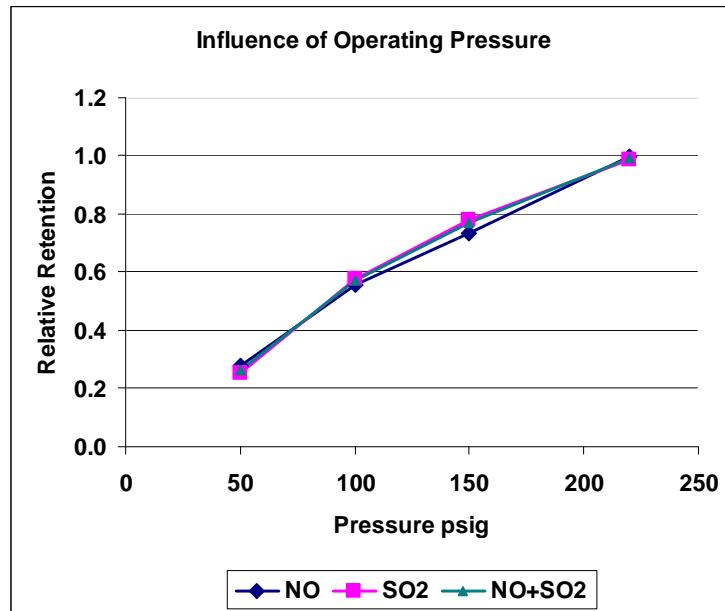
Figure 14. Influence of Operating Pressure on Relative Retention of SOx and NOx

Influence of Operating Pressure
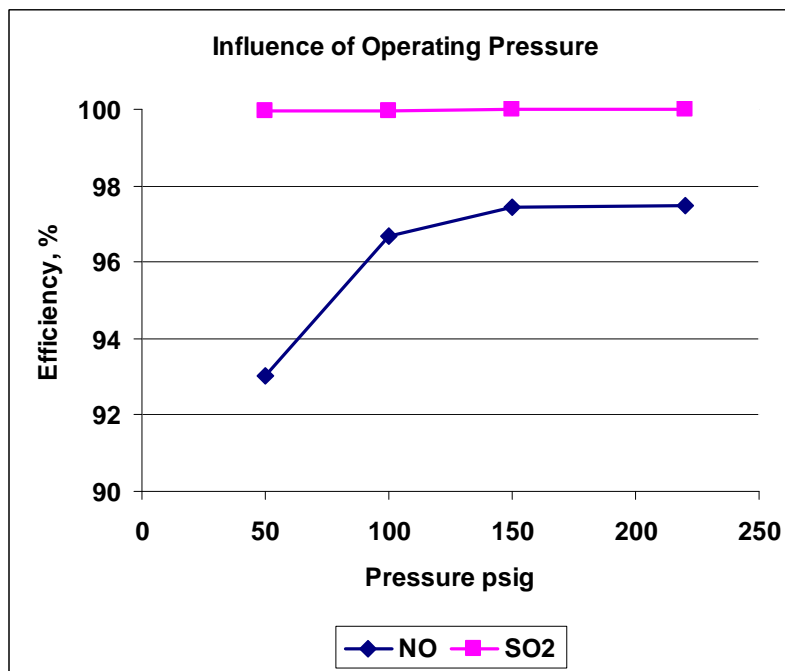
Figure 15. Influence of Operating Pressure on SOx and NOx Removal Efficiencies

Influence of Inlet Composition

Experiments were conducted at different NO/ SO_2 inlet molar ratio in the range of 0 - 0.4 (see Figure 16). It was concluded that within this range a higher NO/ SO_2 molar ratio is beneficial for individual and overall retention capacity of contaminants on activated carbon. This can be attributed to Reaction 9 which shows that there is an enhancement of SO_2 oxidation in the presence of NO_2, while the NO oxidation and adsorption is inhibited

by SO_2 presence. The NO/ SO_2 inlet molar has little effect on SO_2 removal efficiency. A lower NO/ SO_2 inlet molar leads to slightly lower removal efficiency of the NO (see Figure 17).
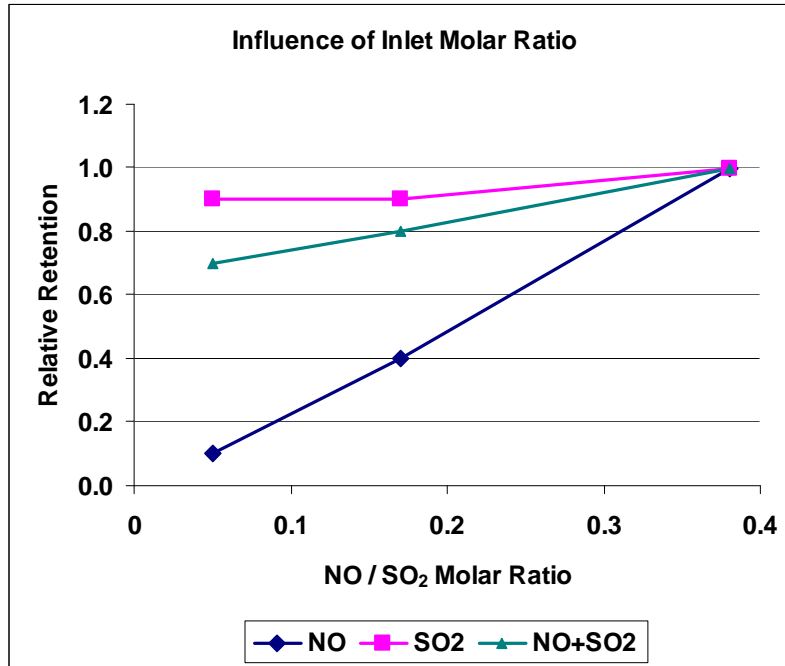
Figure 16. Influence of NO/SO$_2$ Molar Ratio in Feed on Relative Retention
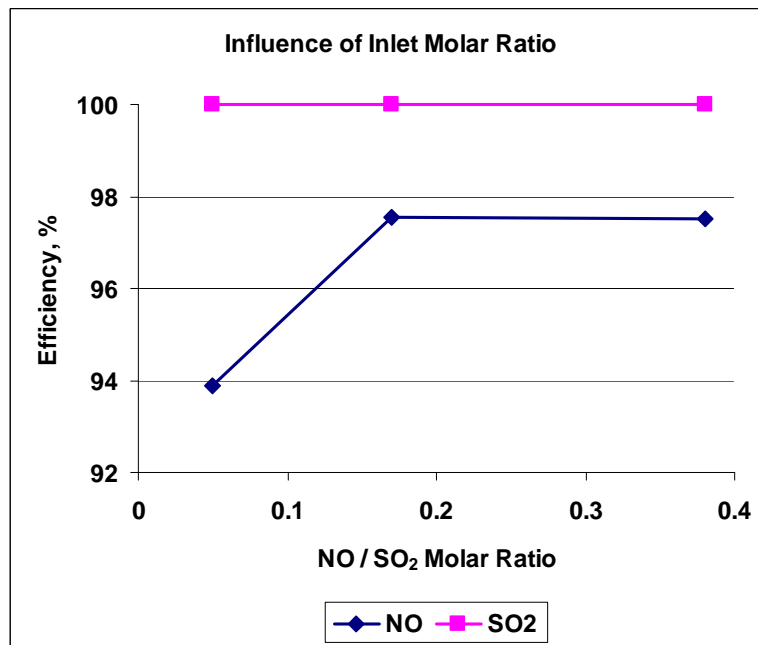
Figure 17. Influence of NO/SO$_2$ Molar Ratio in Feed on Removal Efficiency

Influence of Water

Water presence in the simulated flue gas stream enhances SO_2 removal through Reactions 3-8. Based on the experimental results obtained, it can be concluded that as long as water vapors are present in the feed at a concentration lower or closed to SO_2 concentration, they have a positive effect on simultaneous SOx/NOx removal. Excess water concentration in the gas phase may initiate Reaction 11 which can inhibit the removal of NOx during the adsorption stage.

Influence of residence time

The effect of residence time on the overall retention of the contaminants on the activated carbon bed is not significant. The results indicate that the differences between the retentions for different gas flowrates, and similar temperature, pressure and inlet composition are within the experimental error (see Figure 18).
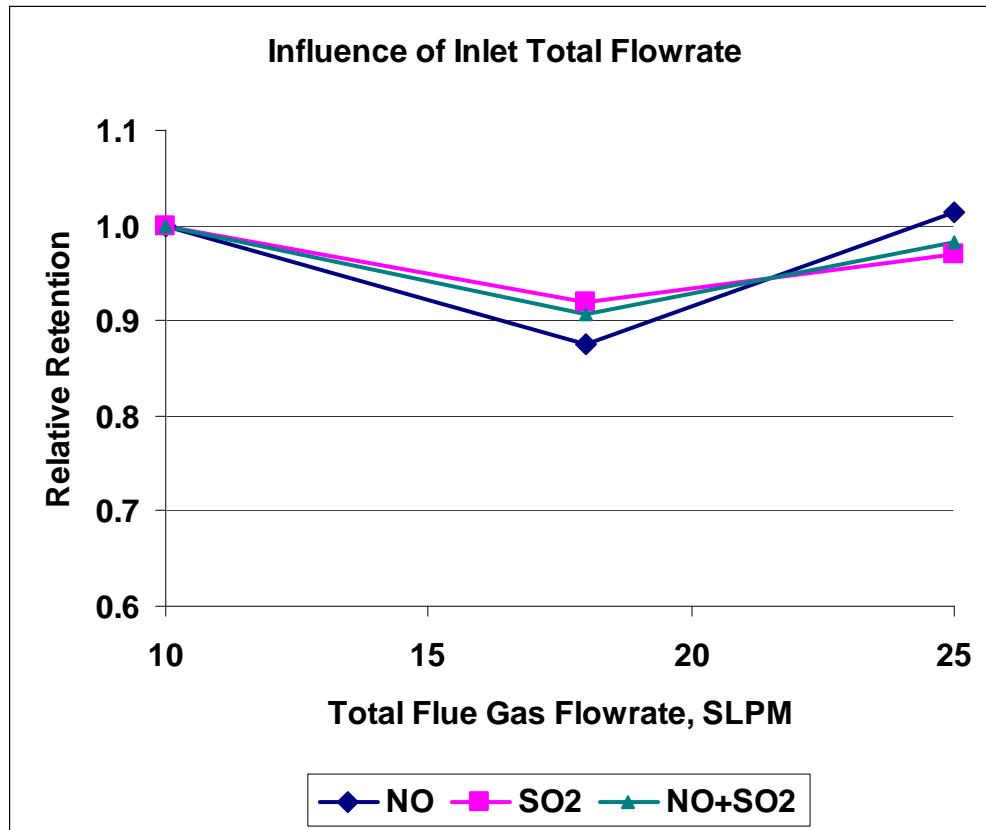
Figure 18. Influence of Total Feed Flowrate on Relative Retention

Waste Water Analysis

Waste water analysis was contracted to IsleChem LLC to determine the content of sulfate, sulfite, nitrate and nitrate for selected experiments using ion chromatography. The results indicate that most of the SOx species (more than 99 %) adsorbed on the activated carbon were found in the waste water stream in the form of sulfates and sulfites. The nitrogen species found the waste water stream are nitrates and nitrates and

correspond to less than 60 % of the NO adsorbed on carbon. This support the findings previously discussed that during the regeneration period part of the NO_2 is converted back to NO.

Material Longevity Investigation

The bench unit was used to briefly investigate material longevity in batch mode operation, by repeating the adsorption regeneration cycles. For this purpose, a carbon bed was exposed to the conditions given for bed 9 in Table 3. After about 20 cycles of adsorption – regeneration, material performance remained unaltered.

Subtask 3.4 – Mercury and Residual NOx Removal Research:

Mercury in the flue gas usually exists in three forms: oxidized (Hg^{2+}, usually as HgCl, HgO, and HgS), elemental (Hg^{o}) and particle-bound (Hg^{p}). Due to its high volatility, mercury usually exists in vapor form. Oxidized mercury is soluble in water and can be removed through its dissolution in water [3]. Relative amount of different mercury forms present in the flue gas depends on coal type and combustion systems. Studies done on pilot and full-scale systems indicated that amount of oxidized mercury ranges from 10-80% of the total vapor phase mercury [4, 5 and 6].

There are three locations where mercury can be captured in the CPU: compression stage, moisture removal stage, and within the activated carbon process stage during the regeneration stage, when the acidic waste water can dissolve most of the mercury left in the gas stream. Additionally, a polishing step using sulfur impregnated activated carbon can be used before the cold box for final mercury removal.

Subtask 3.5 – Continuous Operation Unit

Continuous Unit Construction

The continuous unit is shown in Figure 19. The reactor skid was located in the center of the hood; the supply skid was located at the right end, while the analytical skid is shown at the left end.

The MFCs for gas metering were located at the bottom of the skid, while the liquid SO_2 pump, the water process pump, and water pump for regeneration were mounted at the top of the supply skid. This also contained the humidifier. The water pump for the discharge of the waste water vessel, which can be seen between the analytical and the reactor skid, was mounted at the bottom of the reactor skid. The analyzers were located at the bottom of the analytical skid, while the sample conditioning units for drying the gas samples before sending them to the analyzers can be seen mounted on the upper side of the skid.
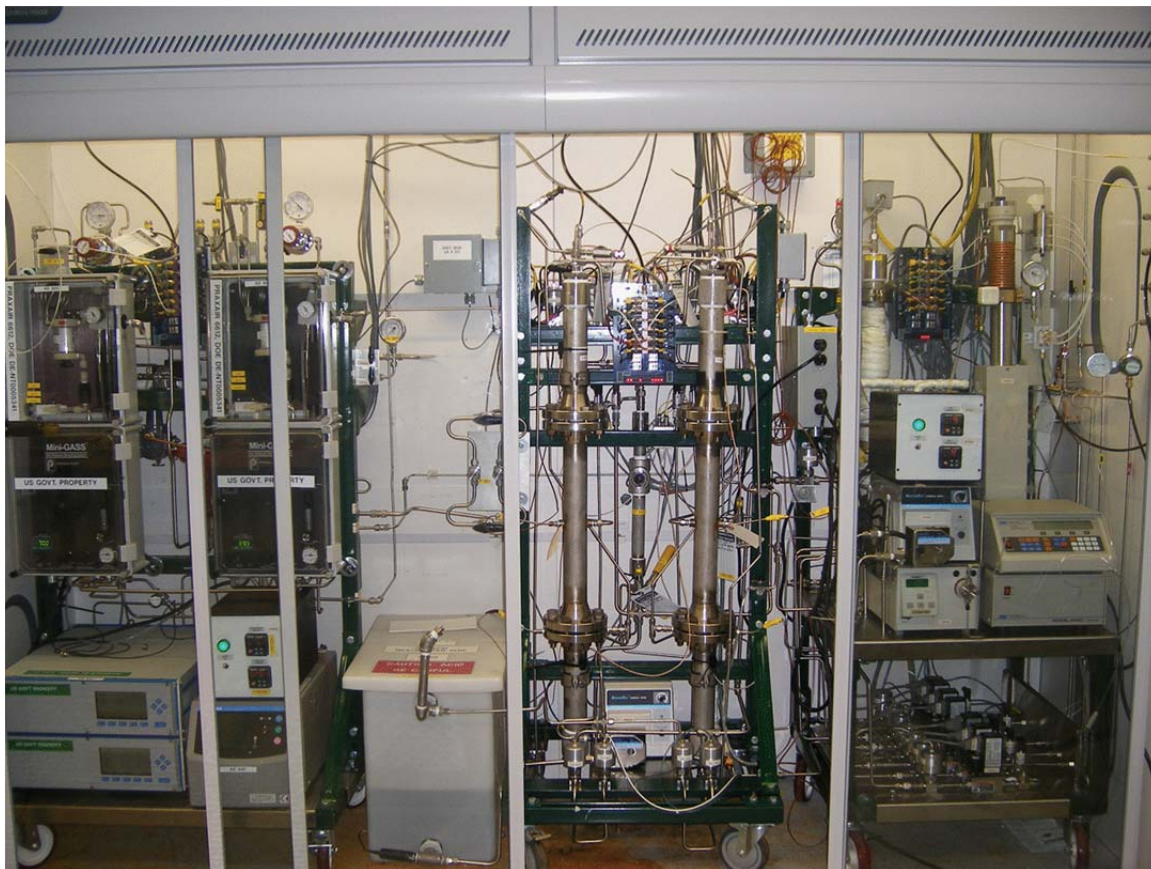
Figure 19. Dual Bed Continuous Operation Unit

Continuous Unit Commissioning

Testing of Regeneration Stage

Regeneration consisted of washing the carbon material with water, to remove the contaminants in the form of their corresponding acids: H_2SO_4, and HNO_3, followed by a drying step to remove the water from the carbon material. The water was fed from bottom to top to avoid channeling and to ensure complete filling of the vessel's volume. The water was kept in the vessel for 10 min to allow enough time for acids formation and their dissolution in the washing water. The waste water was drained pressurizing with nitrogen. Initial tests were conducted to understand the functionality of the regeneration sequence and the required time to complete one regeneration stage.

Figure 20 shows the temperature profile during the regeneration stage. It can be seen that first, due to the depressurization of the bed, the temperature dropped below the ambient. For each water washing step, a slight increase in temperature is observed. This corresponds to the formation of sulfuric and nitric acids which are exothermic reactions. After the washing was completed, nitrogen was flown through the bed for drying. A heating tape was used to preheat nitrogen to 300F before entering the reactor. The temperature profiles depicted in Figure 20 indicate that as water was evaporated the carbon bed started to heat up gradually. A spike in temperature occurred when most of

the water was removed. About 3-4 hours are required for the bed to dry. A cooling period was allowed to avoid starting the adsorption stage with the activated carbon material at temperatures above ambient.
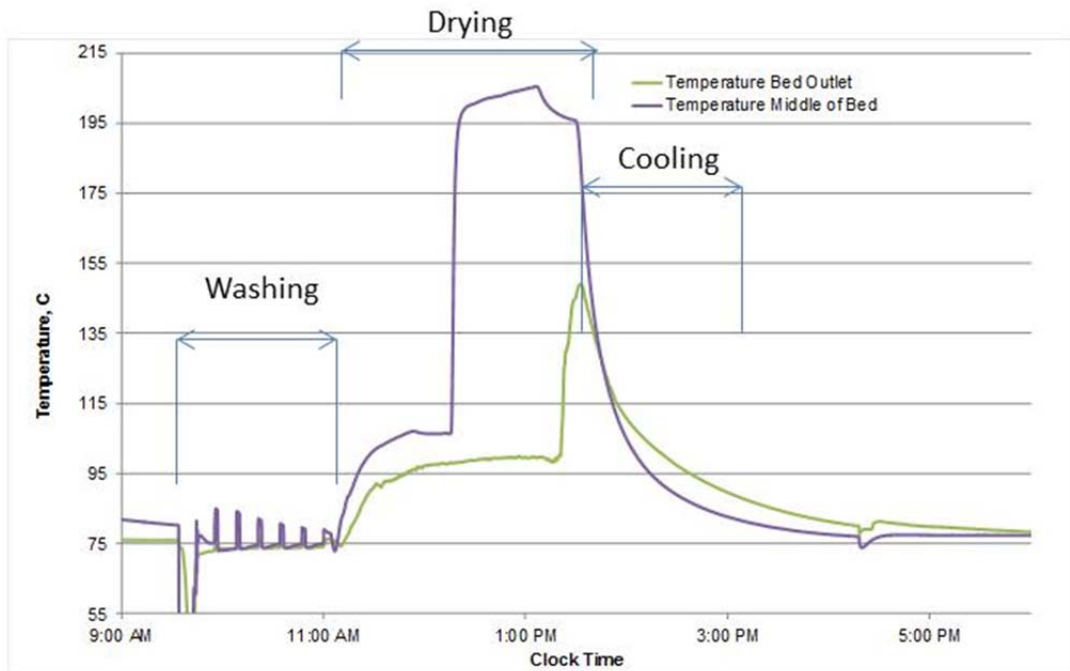
Figure 20. Temperature Profiles During the Regeneration Stage

Samples of waste water were collected for each six discharges. Each sample was analyzed for its content in SO_4^{2-}, and NO_3^- ions in order to understand the efficiency of regeneration. Semi-quantitative colorimetric methods based on a HACH 890 colorimeter (methods 8051, 10020, and 8153) were used.

Figure 21 shows for example the depletion of the sulfate ion concentration with the number of washes. A two order of magnitude decrease was observed. This is an indication of almost complete removal of sulfates through six consecutive washes.
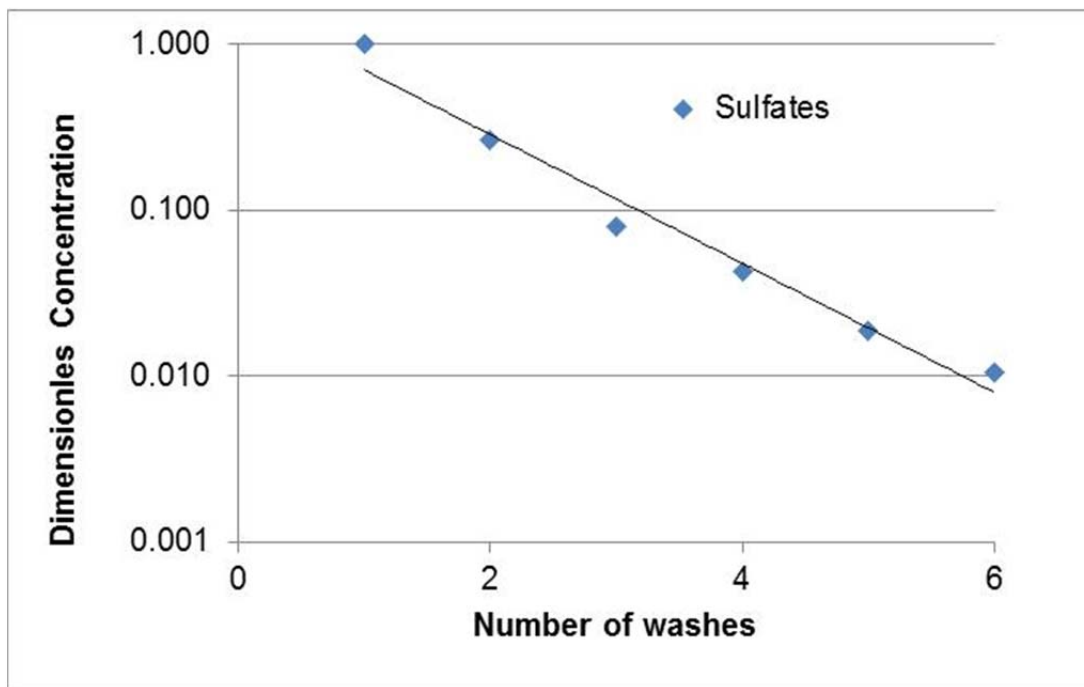
Figure 21. Depletion of Sulfate Ions in Waste Water with the Number of Washes

Testing of Adsorption Stage

The simulated flue gas stream was obtained by mixing the following components: 100% CO_2 (gas), 3% NO in Nitrogen (gas), O_2 100 % (gas) and 100 % SO_2 (liquid). A Teledyne ISCO 500 high pressure high precision pump was used for liquid SO_2 delivery. Several runs using liquid SO_2 as source showed that pumping and vaporizing the SO_2 into the simulated flue gas mixture was challenging. Although the pump had good accuracy, SO_2 flashes within the pump itself leading to uneven flow supply and misleading metering of the amount of SO_2 delivered. Modifications were made to use a gas source of 3% SO_2 in N_2, which gave a more stable feed delivery and composition.

The benchmark evaluation was performed for a simulated flue gas containing: 450 ppm SO_2, 200 ppm NO, 4 % O_2, 94 % CO_2 and N_2 as balance, operating at 220 psig and close to the ambient temperature. The gaseous feed was saturated with water. First adsorption cycle on each bed was carried out for 30 hours each. No breakthrough was observed in this time indicated high level of retention capacity of the carbon. Outlet concentrations of the main components from bed 801 during second adsorption cycle are shown in Figure 22 as a function of running time.
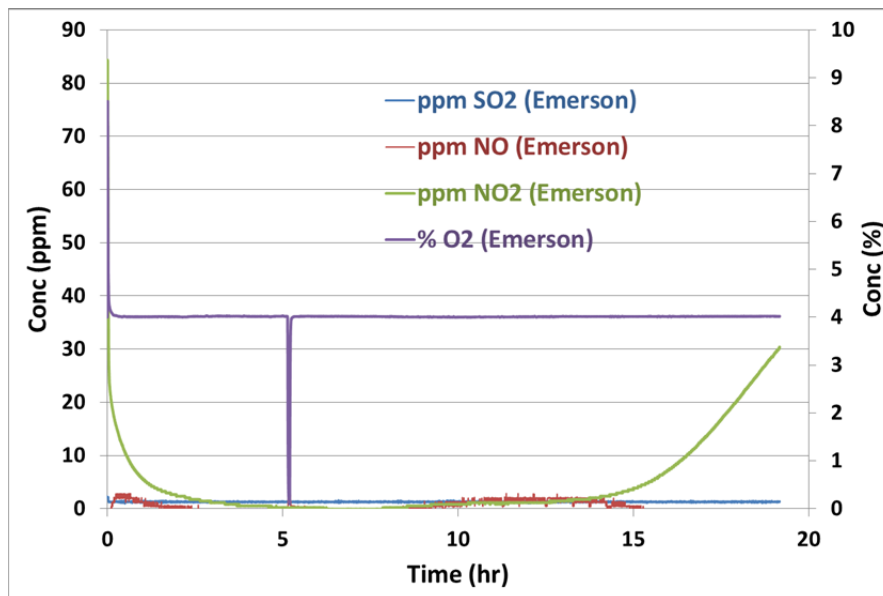
Figure 22. Reactor Effluent Concentrations as a Function of Time

It can be seen that for the selected conditions the breakthrough time is about 19 hours. The SO_2 and NO concentrations in flue gas exiting the reactor remained low below 5 ppm for the whole run, while NO_2 stayed below 5 ppm for ~ 14 hours after which it started to appear at the reactor exit. Thus NO_2 is the first contaminant to breakthrough. For the entire run, SO_2 and NOx (NO + NO_2) removal efficiency was ~100% and ~98% respectively.

During the commissioning and initial experimental tests other operating issues were identified. One important aspect was related to beds depressurization. Sudden pressure release had a severe impact on the activated carbon. Material dusting was observed, most probably induced by gas-solid friction and sudden temperature drop. Modifications were implemented to achieve a gradual change in pressure when the feed was switched between beds, or for shut-down.

Continuous Unit Operation and Material Longevity Testing

In order to study the longevity of the carbon material, adsorption / regeneration cycles (as shown in Table 2) were repeated 24/7 for 40 days. A log of outlet concentrations of main components was maintained to see the impact of repeated cycles on breakthrough time and thus on retention capacity of the carbon. Cycle times were set such that a clear breakthrough of contaminant was observed and beds were switched only after breakthrough occurred. For the purpose of analyzing bed's retention capacity, 30ppm of NO_2 at the reactor exit was used to mark the end of adsorption cycle.

During the entire run of 40 days, SO_2 and NO removal efficiency of ~100% and 97-98% was observed respectively. Figure 23 shows breakthrough time for bed 801 after several repeated adsorption / regeneration cycles. For the first adsorption cycle breakthrough was not seen even after 30hrs of adsorption time (not shown in Figure 23). In the second

cycle, breakthrough time decreased to ~19 hours. It can be observed that during the course of 40 days breakthrough time gradually dropped down from 20 hr to ~10 hr. The drop was steep till 12th cycle after which it was more gradual. Similar results were observed for bed 802.
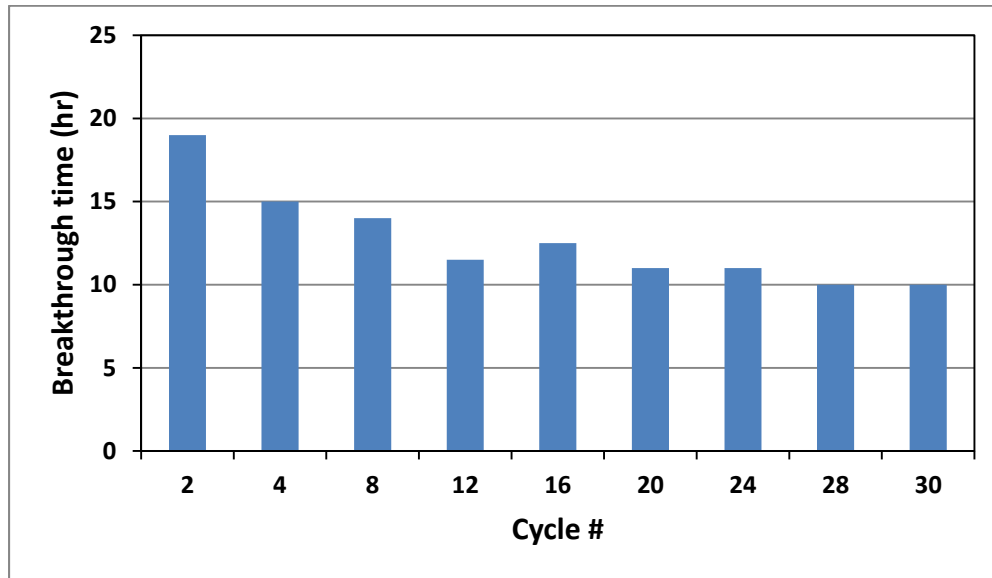
Figure 23. Breakthrough Time for Bed 801

Table 4 shows the removal efficiency of SOx and NOx during adsorption cycles for bed 801. Over 40 day period, removal efficiency of SOx and NOx was >99% and >98% respectively. Similar efficiencies were observed for bed 802.

Table 4. Removal Efficiency for Bed 801 over 40 Days of Continuous Operation

Cycle #	Removal efficiency	
	SOx	NOx
2	99.8	99.1
4	99.9	98.2
8	100	98.5
12	100	97.4
16	100	98.1
20	99.6	98.8
24	99.6	98.9
28	99.4	99.0
30	99.6	98.8

Outlet concentrations of the main components from bed 801 during 30th adsorption cycle (last cycle) are shown in Figure 24 as a function of running time. Breakthrough time dropped to ~10 hours indicating significantly reduced retention capacity of the activated

carbon compared to benchmark. During the entire run SO_2 and NO concentrations in flue gas exiting the reactor remained low below 5 ppm. As seen in the benchmark, NO_2 was the first contaminant to breakthrough and it started to appear at the reactor exit only after ~6 hours but stayed below 10ppm until 9.5 hours. This suggests that despite the reduced retention capacity removal efficiency of the bed was unchanged. SO_2 and NOx removal efficiency was ~100% and ~98% respectively.
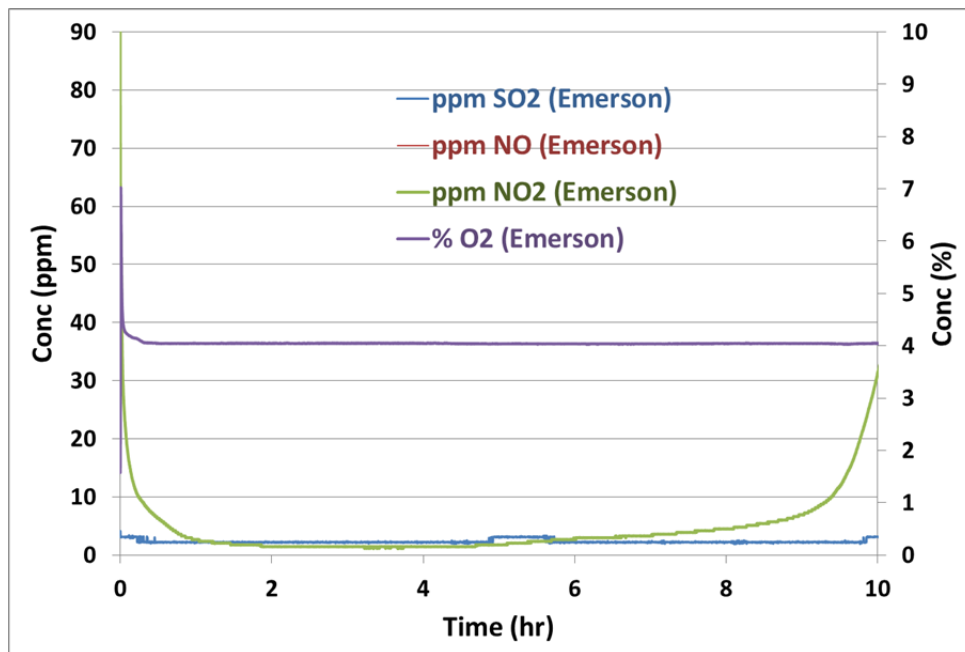

Figure 24. Reactor Effluent Concentration Profiles for 30th Adsorption Cycle

Such drop in breakthrough time was not observed for a feed with 2000ppm SO_2 and 750ppm NO when it was tested on a bench unit for 20 cycles. For each cycle, breakthrough time was ~7.5 hours. When continuous run is compared against the bench scale study, there were several differences in the adsorption and regeneration steps due to differences in relative flow rates, bed volumes and regeneration times. In continuous run, during initial cycles of adsorption carbon bed was exposed to contaminants for very long time. This over exposure might have led to irreversible adsorption of contaminants leading to reduced active sites per unit volume of bed. In the regeneration step, much higher heating temperatures were used in the continuous unit compared to those in the bench scale testing.

In order to verify the structural stability of carbon, a BET analysis was performed. BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyzer. The technique encompasses external area and pore area evaluations to determine the total specific surface area. The BET surface areas of carbon before and after continuous run were 745 m^2/g and 677 m^2/g, respectively. Within the experimental errors this small drop in surface area is negligible. This indicates that the pore structure of carbon was intact during the repeated adsorption-regeneration cycles.

In order to check any irreversible adsorption of contaminants on the carbon surface, ion chromatography was performed on spent carbon. Spent carbon was combusted in a pressurized decomposition vessel with oxygen atmosphere. The combustion gases are scrubbed using a gas washing bottle containing a solution of $NaHCO_3/Na_2CO_3$. The scrubber solution is then analyzed for nitrate and sulfate by ion chromatography. The nitrate and sulfate content of the scrubber solution is used to calculate total nitrate and sulfate content of the carbon sample. It was found that total nitrate and sulfate content of the spent carbon was 3.7% and 2.3% by weight respectively. This indicates that some of the nitrates and sulfates were not removed by water regeneration cycles and ultimately led to drop in retention capacity of the carbon.

Since simple water wash was unable to completely regenerate the carbon sample it was studied that if a thermal re-activation can be used for complete regeneration. In this test, spent carbon was placed in a furnace at 950 ^{o}C under inert atmosphere in order to remove any strongly bound contaminants. It was then subjected to ion exchange chromatography as described above. It was found that even after the thermal reactivation at 950 ^{o}C nitrate and sulfate ions were not removed from the carbon surface. This clearly indicates that the drop in retention capacity of the carbon is due to the irreversible adsorption of nitrates and sulfates and such irreversible adsorption must be avoided.

Hence, further work is needed to optimize adsorption/regeneration cycle in order to maintain carbon bed's high retention capacity for SOx/NOx over a long period of time. This includes:

1. Reduce the cycle time to < 7 hours by increasing feed gas flow or decreasing the amount of carbon. This will reduce the total time of exposure and will limit the adsorption to the surface level.

2. Increase regeneration efficiency by achieving a continuous flow of water through the carbon bed. This will help to remove strongly bound contaminants from the carbon.

3. Eliminate/minimize heating during regeneration step.

Conclusions

Activated carbon process for SOx/NOx removal from simulated oxy-coal flue gas was demonstrated. As proposed, the potential advantages of the Task 3 process is the ability to simultaneously remove SOx and NOx impurities, with high efficiency and eliminate or reduce the need for traditional flue gas purification technologies (FGD and SCR). The following major conclusions can be made: 1) Activated carbon material is suitable for simultaneous SOx and NOx removal at elevated pressures and ambient temperatures; 2) Continuity and scalability of the process is achievable through a multi-bed reactor design 3) Good purification performance can be achieved, more specifically the contaminant content in the stream exiting the purification stage is: SOx <10 ppm, NOx <20 ppm.

The dual bed system was successfully tested with continuous operation for investigating carbon bed's longevity. The overall SOx and NOx removal efficiencies of >99.9% and >98%, respectively, were achieved. The retention capacity of activated carbon material for SOx and NOx was significantly reduced over a long term test period of 40 days. Optimization of adsorption-regeneration cycle is needed to maintain long term activity of activated carbon material at a higher level and thus minimize the capital cost of the system. Minimization of acidic waste water is also required to reduce disposal costs.

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