

PhoSNOX PROCESS FOR COMBINED REMOVAL OF SULFUR DIOXIDE AND NITROGEN OXIDES FROM FLUE GAS

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Keywords: nitric oxide, flue gas cleanup, phosphorus

INTRODUCTION

Wet FGD (flue gas desulfurization) systems are the most widely used technology for control of sulfur dioxide emissions from power plants. However, these systems are incapable of removing nitrogen oxides because most of the nitrogen oxides in flue gas is nitric oxide which is barely soluble in aqueous solutions.

This paper addresses a new and cost-effective method for the generation of ozone to allow a wet scrubber system to remove SO₂ and NO_x simultaneously. In addition, a new method to suppress the formation of nitrogen-sulfur compounds in scrubbing liquors is discussed. The major oxidation product of yellow phosphorus is phosphoric acid mists which can be recovered for byproducts credit. The size of mists and the concentration of phosphoric acid in the mists were measured in order to determine an appropriate device for acid collection and concentration. An economic projection of the PhoSNOX process has been performed.

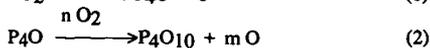
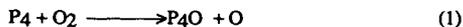
EXPERIMENTAL

The experiments were conducted on a 600 liter/min bench-scale spray tower absorber. A simulated flue gas mixture with about 5% oxygen was prepared by passing liquid nitrogen through a vaporizer column and by mixing the gas with compressed air to obtain the desired oxygen concentration. NO and SO₂ were blended in to give concentration of 60-600 ppm and 1500-2500 ppm, respectively. CO₂ concentration could be adjusted up to approximately 10% of the total gas flow. The gas stream flowed at a rate of 600 liter/min through an electric air heater where it was heated to a temperature of 450 K (350 F). The heated gas then entered a spray tower absorber. The absorber was a 10 cm diameter by 120 cm long glass column installed with spray nozzles (Figure 1). A scrubbing liquor, which was composed of an aqueous mixture of yellow phosphorus was sprayed in the absorber. The liquid flow rate ranged between 1 and 4 gallons/min. A 2-liter Erlenmeyer flask was used as a holding tank for the liquid mixture from the spray column. The liquid mixture was recirculated with a centrifugal pump to the top of the spray column. The pH of the scrubbing liquor was controlled by feeding an aqueous mixture of sodium sulfite or calcium carbonate from a thermostated reservoir (55 C) to the hold tank by a Masterflex pump. The pH range studied was 4.5 to 7.5. The holding tank temperature was controlled at 55 C. A countercurrent flow of flue gas entered at the base of the absorber and passed upward through the falling spray of liquors. The superficial velocity of flue gas in the absorber is about 4 ft/sec. The contact time of flue gas with spraying solution was approximately 2 seconds. The contact time can be varied by changing the flow rate of flue gas; correspondingly, this would vary the L/G ratio, given a constant liquid flow rate. The SO₂ fluorescent analyzer and the NO_x chemiluminescent analyzer have intake connections to the gas stream at various points along the system. The SO₂, NO, and NO₂ concentrations can thus be measured and the effectiveness of the absorber operation can be evaluated.

The major oxidation product of P₄ is phosphoric acid mists which can be recovered as a valuable commercial product. Experiments were performed to determine the size distribution of mists in order to determine an appropriate collector for use in scale-up tests. The size of mists was measured by means of a cascade impactor and a laser optical particle counter. The mists produced from the bench-scale spray tower flowed through thermostated tubings. Then, the mists were sucked into a Mark V Pilat Cascade Impactor, which was installed inside an oven at a controlled temperature. The application of the laser optical particle counter has limitations in that it can not measure particles with size less than 0.5 um, nor can it measure particles with density more than 10⁶ particles/ml. Consequently, the dilution of phosphoric acid mists with air is sometimes necessary. A stream of conditioned mists was allowed to pass through a measuring port of an Insitac PCSV-P laser optical particle counter. The size distribution of the mists was determined from the scattering light of a laser beam. In addition, a mist collector using the impactor and capillary action principles was constructed. The phosphoric acid mists were collected. The concentration of phosphoric acid in the mists was determined by an ion chromatography.

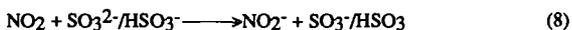
RESULTS AND DISCUSSIONS

The removal of NO from flue gas in the PhoSNOX process is based on the P₄-induced oxidation of NO to produce more soluble NO₂. The chemistry involved can be described by the following reactions:





P₄ reacts with O₂ to produce O and O₃ according to reaction (1) thru (3). Subsequently, O and O₃ oxidize NO to NO₂. NO₂ can be removed by scrubbing liquors through direct dissolution (6), by dissolution after forming N₂O₃ with NO (7), or by reaction with SO₃²⁻ or HSO₃⁻ ion (8).



The presence of SO₃²⁻/HSO₃⁻ at a concentration of greater than 1 mM in scrubbing liquor can cause² most of the NO₂ to react via (8) rather than (6). Consequently, most of the dissolved NO₂ is initially converted to HNO₂.

1. Removal Efficiency

The results of typical runs on the removal efficiency of NO are shown in Figure 2. Greater than 95 % NO removal efficiency were achieved at initial NO concentrations ranging from 58 to 610 ppm with an L/G of 16 liter/m³ and a gas-droplet contact time of about 2 sec. The flue gas was under continuous flow conditions, whereas the P₄ reagent was under batch conditions with a limited amount of P₄ in the circulating liquors. The concentration of P₄ decreased with time, which resulted in the drop of NO removal efficiency. The removal efficiencies of SO₂ were greater than 95 % in these experiments, but were deleted from the figures to avoid confusion.

The NO removal efficiencies as a function of L/G and P₄ concentration in spray liquors are shown in Figure 3. The results were obtained from a set of experiments which were conducted by varying the flow rate of flue gas at a constant flow rate of recycling liquors. As a result, the contact time of the flue gas with the spray varied. The removal efficiency did not reach 90% until an L/G of 10 liter/m³ with spray liquors of 0.5% P₄ concentration. The increase of P₄ concentration from 0.5% to 0.8% reduced the required L/G from 10 liter/m³ to 8 liter/m³ in order to achieve a 90% NO removal efficiency.

Because the diameter of the spray column is 4 inches, the droplets hit the wall a short distance after being sprayed. The liquor then flows down the wall of the column and exhibits poor contact with flue gas. Consequently, the mixing in the bench-scale system is not as effective as that in a commercial scale system at a given L/G. The consideration of the contact time of the droplets with flue gas may be more meaningful. Figure 4 shows a plot of the NO removal efficiencies as a function of contact time. The gas-droplet contact distance was estimated to be 2 ft. The contact time can be varied by changing the flow rate of the flue gas. The NO₂ removal reached 90% efficiency with a contact time of 1.4 secs, which is less than that (2-5 secs) in a commercial system. However, it must be realized that the size of the droplets is smaller than those in a commercial system. Consequently, the mass transfer from gas to liquid is more effective in our bench absorber than in a commercial absorber. The utilization efficiency of P₄ can be expressed in terms of P/NO ratio. A P/NO ratio of as low as 0.6 has been achieved.

2. Byproducts Formation

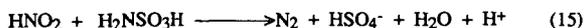
The analysis^{3,4} of scrubbing liquors from a bench-scale experiment revealed that less than 10% of the NO removed was converted to NO₃⁻. The majority of NO removed was found to be in the form of nitrogen-sulfur compounds, which were produced as a result of the reaction of NO₂⁻ with HSO₃⁻



These nitrogen-sulfur compounds can be converted to ammonium sulfate under extremely acidic conditions



Alternative ways to remove the nitrogen-sulfur compounds from scrubbing liquors include the precipitation as potassium salts and the use of an electrodialysis technique. We have recently developed a new approach to suppress the formation of the aforementioned nitrogen-sulfur compounds. This approach involves the use of a sulfamic acid additive which can be produced from the reaction of urea and sulfuric acid. As a result of the addition of sulfamic acid in scrubbing liquors, the absorbed NO is converted to N₂.



The majority of yellow phosphorus was oxidized by oxygen in flue gas to form P₄O₁₀, which subsequently absorbed moisture to form phosphoric acid mists. The analysis of spraying liquors by ion chromatography showed that only about 10% of these mists were absorbed into scrubbing liquors. The remaining 90% of mists stayed with the flue gas, as evidenced by its heavy white appearance. These mists must be removed from flue gas so that a valuable by-product, phosphoric acid, could be recovered and that the flue gas discharged from a stack could comply with opacity regulations.

3. Characterization of Phosphoric Acid Mists

The size distribution of the mists was determined in order to choose an appropriate collection device for the mists. Two different techniques, a cascade impactor and a laser optical particle counter, were employed to measure the size of mists for comparison. The results obtained from these two techniques are in good agreement. Table 1 shows that the geometric mean diameter of mists increases from 0.65 μm to 1.1 μm as the residence time extends from 0.7 sec to 11 sec. The size of the mists increases along with the residence time of the mists, which was attributed to the coagulation. However, a small decrease of temperature during the transit of the mists may result in the grow of the size from the condensation of moisture in spite of the temperature control along the pathway of the mists. The size distribution of the mists, in terms of mass frequency vs size, was measured by the optical particle counter. The size distribution of the mists peaked at 0.5 μm, 0.9 μm, and 1.2 μm with a residence time of 0.7, 5.6, and 11.2 sec, respectively.

The concentration of phosphoric acid in the mists was about 10% by weight. This was determined by the collection of the mists with a sinter glass impactor. The solutions soaked in the sinter glass was sucked into a container through a capillary tube. The solutions collected was analyzed by an ion chromatography.

From the results of size and concentration measurements, the use of a submicron mist collector such as an Aerosep multi stage aerosol separation system may be necessary to recover the phosphoric acid mists. The residence time of phosphoric acid mists in a prescrubber or a scrubber is expected to be less than 5 sec. As a result, a substantial fraction of the mists is less than 1 μm. In addition, the acid recovered has to be concentrated to about 75 wt % in order to produce a marketable byproducts.

4. Process Configuration

A conceptual process configuration of a wet PhoSN₂O_x system with throw-away wastes may be derived as shown in Figure 5. An aqueous mixture of P₄ and an alkaline reagent such as limestone or soda ash may be sprayed in a scrubber. A mist collector is required to recover the phosphoric acid mists to comply with the opacity regulation and for by-product credit. An air-purged oxidation tank is installed to ensure the complete conversion of residual P₄ to phosphate ions before discharge. Besides the addition of a mist collector and an air-purged oxidation tank, this is a typical process configuration of a throw-away wet flue gas desulfurization system.

An alternative process configuration (Figure 6) may be derived where an aqueous mixture of P₄ and sulfamic acid is injected into a prescrubber or a section of the duct upstream from the scrubber where an alkaline solution/slurry is used to absorb acid gases. An Aerosep mist collector is installed between the prescrubber and the scrubber. A slip stream of liquor from a scrubber loop was fed into a prescrubber loop to ensure the conversion of absorbed NO_x to N₂.

5. Process Economic Projection

Pre-pilot plant economic projections for the PhoSN₂O_x process have been made based on a preliminary conceptual process configuration with the following features:

- Injecting a phosphorus emulsion into an existing wet limestone scrubber, or injecting an aqueous mixture of yellow phosphorus and sulfamic acid into a new prescrubber
- Adding an "Aerosep" system downstream of the scrubber (or prescrubber) to capture and convert the P₂O₅ to phosphoric acid byproduct
- Installing necessary equipment to recover other phosphate byproducts
- Adding new fan capacity to compensate for the additional pressure drop
- Adding new equipment for phosphorus and byproducts storage
- Installing fire & safety protection equipment on phosphorus unloading, storage, and handling system.

The PhoSN₂O_x process economics are compared with those reported in the literature for the Selective Catalytic Reduction (SCR) process, as shown in Table 2.

CONCLUSION

The PhoSNOX process is based on the addition of yellow phosphorus in wet flue gas desulfurization systems to allow simultaneous removal of SO₂ and NO_x from flue gas. The NO_x removal efficiency of PhoSNOX at 90+% could potentially be achieved at the actual conditions employed in wet FGD systems. Pre-pilot plant economic projections for the PhoSNOX process indicates that the capital installation costs for PhoSNOX are lower and operating costs are comparable when the process is compared with SCR.

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Table 1 Comparison of the Mean Diameters of Mists from Laser Scattering and Cascade Impactor Measurements

Methods		Residence Time(sec)		
		2.8	6.5	11.2
Laser	0.66 um	0.72 um	0.97 um	1.10 um
Impactor	0.67 um	0.67 um	0.83 um	

Table 2. Economics Comparisons: NO_x Removal Processes (500 MW, 300 ppm NO_x)

	Capital, \$/kW	Levelized, mills/kWh
PhoSNOX (90% NO _x Removal; P/NO _x =0.5)		
W/O prescrubber	28	4.2
With prescrubber	43	4.7
SCR (80% NO _x Removal)		
EPRI (1991 NO _x Symposium Summary)	100	5 - 7
EPRI (1989 NO _x Symposium Summary)	78 - 101	4 - 9

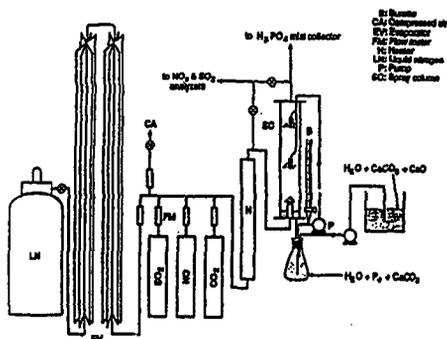


FIGURE 1. A schematic diagram of a 20 cfm (0.44 x 10⁻¹ m³/sec) bench-scale wet scrubber using yellow phosphorus and an alkaline for combined removal of SO₂ and NO_x from a simulated flue gas.

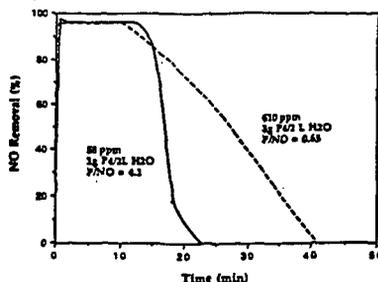


FIGURE 2. The removal efficiency of NO for NO concentrations of 88 and 610 ppm in a simulated flue gas.

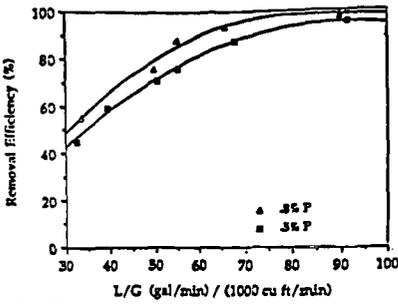


FIGURE 3. The removal efficiency of NO as a function of L/G [$1 \text{ liter/m}^3 = 7.48 \text{ gal}/1000 \text{ cu ft}$] with initial yellow phosphorus concentration of 0.5% and 0.8%.

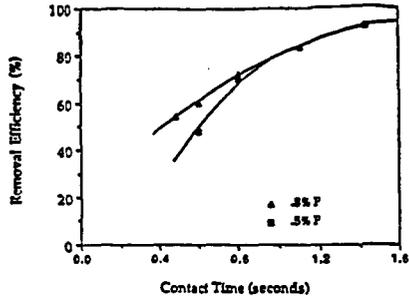


FIGURE 4. The removal efficiency of NO as a function of the contact time of spray droplets with a simulated flue gas.

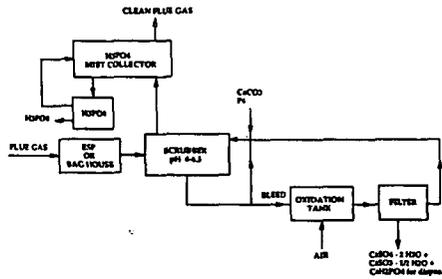


Figure 5 A conceptual process configuration of a wet PhoNOX system with throw-away wastes

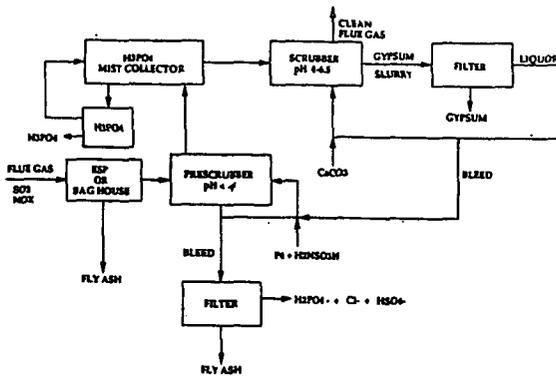


Figure 6 A conceptual process configuration of a wet PhoNOX system with salable byproducts