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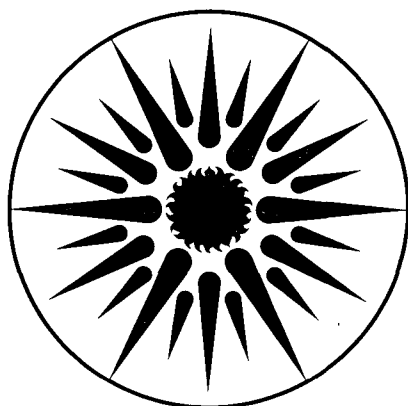
## APPLIED SCIENCE DIVISION

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## DEVELOPMENT OF LBL PHOSNOX COMBINED NO<sub>x</sub>/SO<sub>2</sub> TREATMENT PROCESS

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### Introduction

The LBL PhoSNOX process is a new advanced flue gas treatment process with the potential for removing more than 95% of both NO<sub>x</sub> and SO<sub>2</sub> from flue gas. The initial idea of the process was conceived in 1987. The process uses yellow phosphorus (P<sub>4</sub>) to induce the oxidation of insoluble NO to NO<sub>2</sub>. P<sub>4</sub> reacts with flue gas O<sub>2</sub> to produce ozone which selectively oxidizes NO to NO<sub>2</sub>. Subsequently, NO<sub>2</sub> and SO<sub>2</sub> are removed from flue gas by dissolution into an aqueous alkaline solution/slurry. P<sub>4</sub> is converted to a desirable commercial by-product, phosphoric acid, as a result of this interaction.

Laboratory experiments were conducted in 1987 and 1988, and their results were extremely promising<sup>1,2</sup>. The experiments were carried out in a bubbling absorber column that was 2 inches in diameter using 200 ml of reaction mixture. The gas flow rate was about 0.035 cfm, corresponding to a superficial velocity of flue gas of 0.0028 feet per second in the absorption column and a contact time of flue gas with scrubbing liquors of approximately 12 sec. However, in a commercial scrubber system, the superficial velocity of flue gas was much faster (4-12 feet per second) and the contact time much shorter (0.25-5 seconds). Consequently, the mass transfer and chemical reaction kinetics were less favorable under the conditions of a commercial system.

To determine whether the new approach was effective in realistic conditions, we conducted experiments in a 20 cfm bench-scale scrubber system. This system was constructed to simulate, as close as possible, the conditions of a commercial system in 1989. The bench-scale system used a column (4 inches in diameter and 4 feet long) as an absorber. Two types of absorbers were examined - one containing spray nozzles to simulate a conventional spray tower absorber, and the other simulated a Chiyoda bubbling absorber. (The scaled-down version of the Chiyoda absorber was designed by George Lee of Bechtel Corporation.) The flue gas entered the Chiyoda absorber downward through impingers that submerged 10 inches under the scrubbing liquor. The superficial velocity was about 4 feet per second, and the contact time was about 0.2 seconds. (These values were typical of a commercial Chiyoda-121 scrubbing system.) A simulated flue gas mixture with about 5% oxygen was prepared by mixing evaporated liquid nitrogen with compressed air. NO, SO<sub>2</sub>, and CO<sub>2</sub> were blended into the mixture and heated to about 150 °C before flowed through the scrubbing system. We studied the removal efficiency of NO and SO<sub>2</sub> as a function of L/G<sup>3</sup>. We found that more than 90% of NO removal efficiency could be achieved with an L/G > 60 (gal/min)/(1000 cu ft/min). Most of the experiments were carried out with a NO concentration of around 300 ppm.

During the past year, parametric studies of the NO removal efficiency and the P/NO stoichiometric ratio were carried out with the 20 cfm bench-scale system. The parameters studied included the concentrations of NO in flue gas and P<sub>4</sub> in spraying liquors. The fate of NO<sub>x</sub>, SO<sub>2</sub>, and P<sub>4</sub> was investigated. Computer modelings of the NO<sub>x</sub> and SO<sub>2</sub> removal efficiencies and chemistry of nitrogen-sulfur compounds in scrubbing liquors were performed. A revised process configuration was proposed, and a mass balance of nitrogen, sulfur and phosphorus was made. An updated process economical evaluation was performed by George Lee of Bechtel Corporation. A safety evaluation was conducted by FMC. Pilot plant tests involving Bechtel Corp. and FMC were planned.

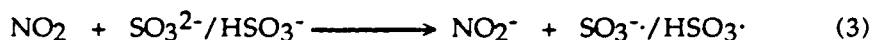
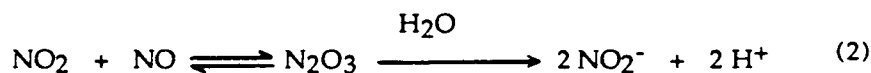
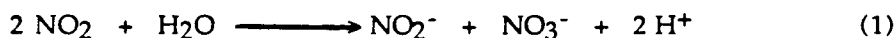
This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Utilization Systems, U.S. Department of Energy under contract No. DE-AC03-76F00098 through the Pittsburgh Energy Technology Center, Pittsburgh PA.

## Results and Discussions

Figure 1 and 2 show that greater than 95% NO removal efficiency was achieved at three initial NO concentrations: 58, 300, and 610 ppm. These experiments were performed under continuous flue gas flow conditions, but under P<sub>4</sub> batch conditions with a limit amount of P<sub>4</sub> in the circulating liquors. The concentration of P<sub>4</sub> decreased with time, which resulted in the drop of NO removal efficiency. The initial SO<sub>2</sub> concentration was 1500 ppm. The removal efficiency of SO<sub>2</sub> was greater than 90% in all three cases, but was deleted from the figures to avoid confusion. Figure 2 showed that the P/NO ratio was better when dilute P<sub>4</sub> concentration was employed. However, the NO removal efficiency may not have reached a desirable value if the P<sub>4</sub> concentration was too dilute. Consequently, one had to maintain enough P<sub>4</sub> concentration in liquors to achieve a desirable NO removal efficiency, but not too much P<sub>4</sub> so that the waste of P<sub>4</sub> could be avoided. A P/NO ratio as low as 0.6 was achieved with the 20 cfm bench-scale absorber.

The fate of P<sub>4</sub>, NO<sub>x</sub>, and SO<sub>2</sub> were examined. P<sub>4</sub> was oxidized by O<sub>2</sub> from flue gas to form P<sub>4</sub>O<sub>10</sub>, and P<sub>4</sub>O<sub>6</sub>, which subsequently absorbed moisture to form H<sub>3</sub>PO<sub>4</sub> and H<sub>3</sub>PO<sub>3</sub> mists. The analysis of spraying liquors by ion chromatography showed that only about 10-15% of these mists were absorbed into scrubbing liquors in a spray tower configuration. Presumably, the remaining 90-85% of mists stayed with the flue gas, as evidenced by its heavy white appearance. A high efficiency mist collector, such as a Brink separator, was required to remove the remaining mists from flue gas so that a valuable by-product, phosphoric acid, could be recovered and so that the flue gas discharged from a stack could comply with opacity regulations. Analytical results also revealed that the concentration ratio of H<sub>3</sub>PO<sub>4</sub> and H<sub>3</sub>PO<sub>3</sub> is roughly 9 to 1; a trace amount of H<sub>3</sub>PO<sub>2</sub> were detected.

NO is oxidized rapidly by ozone, produced from the P<sub>4</sub> and O<sub>2</sub> reaction, to form NO<sub>2</sub>. NO<sub>2</sub> can be removed by scrubbing liquors through direct dissolution (1), by dissolution after forming N<sub>2</sub>O<sub>3</sub> with NO (2), or by reaction with SO<sub>3</sub><sup>2-</sup> or HSO<sub>3</sub><sup>-</sup> ion (3).



The presence of HSO<sub>3</sub><sup>-</sup>/SO<sub>3</sub><sup>2-</sup> at a concentration of greater than 1 mM in scrubbing liquor, which is typical in wet limestone/lime systems, can cause most of the NO<sub>2</sub> to react via (3) rather than (1). Consequently, most of the dissolved NO<sub>2</sub> is initially converted to HNO<sub>2</sub>. The analysis of scrubbing liquors from a bench-scale experiment revealed that less than 10% of the NO removed was converted to HNO<sub>3</sub>. The majority of NO removed was found to be in the form of a nitrogen-sulfur compound, hydroxylamine disulfonate (HADS), which is formed by the reaction of NO<sub>2</sub><sup>-</sup> with HSO<sub>3</sub><sup>-</sup>



HADS can undergo further sulfonation and/or hydrolysis to form other nitrogen-sulfur compounds<sup>4</sup>. Nevertheless, it is expected that HADS is the major nitrogen-sulfur compound present in the scrubbing liquor. These nitrogen-sulfur compounds can be removed from scrubbing liquors either through precipitation as potassium salts or via hydrolysis to form NH<sub>4</sub>HSO<sub>4</sub> under acidic conditions. The potassium salts of nitrogen-sulfur compounds can be thermodecomposed to form N<sub>2</sub>, NH<sub>3</sub>, and K<sub>2</sub>SO<sub>4</sub>,

of which the latter reagent can be recycled. The solubility and thermo-decomposition behavior of potassium salts of nitrogen-sulfur compounds were studied.<sup>5</sup>

Initially,  $\text{SO}_2$  was converted to  $\text{HSO}_3^-/\text{SO}_3^{2-}$  after dissolution. Some of the  $\text{HSO}_3^-/\text{SO}_3^{2-}$  underwent electron transfer with  $\text{NO}_2$  to yield free radicals  $\text{HSO}_3/\text{SO}_3^-$ ; most of these radicals subsequently reacted with flue gas  $\text{O}_2$  to produce sulfate. Some of the  $\text{HSO}_3^-/\text{SO}_3^{2-}$  reacted with  $\text{NO}_2^-$  to form nitrogen-sulfur compounds; the sulfur associated with these compounds can be converted to sulfate regardless of whether the precipitation or hydrolysis route is chosen for separating them from scrubbing liquors. The remaining  $\text{HSO}_3^-/\text{SO}_3^{2-}$  may be oxidized by flue gas  $\text{O}_2$  to produce sulfate. Sulfate can be precipitated as gypsum.

Computer modeling<sup>6</sup> of the solution kinetics occurring in the scrubbing liquors was performed using a chemical kinetics program on Macintosh computer with a Fortran 77 compiler. Chemical reactions and their rate constants were symbolically entered into the program. The program converted the input into ordinary differential equations in a matrix format. An ordinary differential equation solving package developed by C.W. Gear was incorporated into the program. The program provided output in the form of concentrations vs. time of the chemical species involved in the reactions used. This output can be used to develop profiles of concentrations vs. time. The model currently does not include mass transfer factors for the gas to liquid transfer process. However, a comparison between experimental measurements of the reaction of nitrite ion with bisulfite ion, under a range of conditions similar to those found in flue gas scrubbers, and calculations of the reactions by the computer model showed good agreement. Transfer of  $\text{SO}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$  from the gas phase to solution was simulated by assuming that conditions were suitable for absorption of approximately 90% of the  $\text{SO}_2$  in the gas phase into solution. The absorption of  $\text{NO}$  and  $\text{NO}_2$  from the gas phase into solution was determined from the  $\text{SO}_2$  absorption using the Henry's constants and the gas phase concentrations of the three compounds. This allowed calculation of the percent removal of  $\text{NO}$  and  $\text{NO}_2$ .

The model indicated that, in spite of having a lower gas phase concentration and lower solubility than  $\text{SO}_2$ ,  $\text{NO}_2$  removal efficiency was high. For a counter-current flow absorber, the following removal efficiencies were calculated:

$\text{SO}_2$	91%	$\text{NO}_2$	91%	$\text{NO}$	2%
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Since almost all of the  $\text{NO}$  is oxidized to  $\text{NO}_2$  by the PhoSNOX process, the  $\text{NO}_x$  removal efficiency is high.

In the simulation, the scrubbing liquor is in contact with the flue gas for 3 seconds before being sent to the hold tank for 300 seconds. Make-up quantities of the reagents are then added to the scrubbing liquor before the cycle is repeated. The concentration profiles of the nitrogen-sulfur compounds in the scrubbing liquor as a function of time are shown in Figure 3. The simulation conditions used were  $[\text{SO}_2] = 2500$  ppm,  $[\text{NO}] = 400$  ppm,  $[\text{NO}_2] = 40$  ppm with the scrubbing liquor containing 10% (wt)  $\text{CaCO}_3$ , 1% (wt)  $\text{CaSO}_4$ , 0.1M  $\text{SO}_4^{2-}$ , and 0.03M sulfite/bisulfite at pH 5.5, 50°C, and L/G = 60. Besides HADS, the nitrogen-sulfur compounds shown in the figure are hydroxylamine monosulfonate (HAMS), amine trisulfonate (ATS), and amine disulfonate (ADS). The concentrations shown are for one cycle through the absorber and hold tank.

A revised conceptual process configuration was proposed (Figure 5) with the following characteristic features: 1. A prescrubber was added for injecting an aqueous  $\text{P}_4$  emulsion to induce  $\text{NO}$  oxidation to  $\text{NO}_2$ , 2. A Brink mist collector was installed between a prescrubber and a scrubber to collect phosphoric acid mists, and 3. A slip stream of liquor from a scrubber loop was fed into a prescrubber loop to increase the hydrolysis rate of nitrogen-sulfur compounds due to the acidic nature

of liquors in the prescrubber loop. A mass balance of phosphorus, sulfur, and nitrogen species in mole/min was indicated on the figure, which were calculated based on the following conditions: Flue gas initially contained 3000 ppm SO<sub>2</sub>, 300 ppm NO<sub>x</sub> (95% NO and 5% NO<sub>2</sub>), and 80 ppm HCl. The removal efficiency of Cl<sup>-</sup> and H<sub>3</sub>PO<sub>4</sub> mists in the prescrubber was 90% and 10% respectively. The remaining 90% of H<sub>3</sub>PO<sub>4</sub> mists was collected in the Brink mist collector, while the remaining 10% of HCl was captured in the scrubber. The removal efficiency of SO<sub>2</sub> and NO<sub>x</sub> in the scrubber was 95% and 90% respectively. 10% of NO<sub>x</sub> removed was converted to HNO<sub>3</sub> and 90% of which was initially converted to HNO<sub>2</sub>, and then reacted with HSO<sub>3</sub><sup>-</sup> to form nitrogen-sulfur compounds. The stoichiometric ratio P/NO of 0.5 was assumed.

Updated economic projections for the PhoSNOX process have been made based upon the aforementioned conceptual process configuration with the following features:

- Injecting a phosphorus emulsion into a new prescrubber,
- Adding a "Brink" separator/hydrator (or equivalent) downstream of the prescrubber to capture and convert the P<sub>2</sub>O<sub>5</sub> 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.

The operating cost of this process is sensitive to the required P/NO<sub>x</sub> molal ratio, the NO<sub>x</sub> removal requirement, and the obtainable byproduct credits. The process economic projections are summarized in Table 1. The estimated capital investment would be in the range of \$34-37/KW. The levelized control costs are 4.6 to 6.8 mills/kWh for a 90% NO<sub>x</sub> reduction, and 3.4 mills/kWh for 50% NO<sub>x</sub> reduction. These estimated costs compare favorably with SCR for high removal, and are competitive with urea injection for low removal.

The PhoSNOX process economics can be improved under the following conditions: 1) lower P/NO<sub>x</sub> ratio required for a given removal efficiency, 2) higher obtainable byproduct credit. The first condition can be determined only with further pilot plant testing. The second condition requires more work in market research. The byproduct value of \$300/ton P<sub>2</sub>O<sub>5</sub> used in this study is conservative. A range of byproduct values has been used for cost sensitivity analysis. The results are shown in Figure 4.

To further improve the process economics, we are looking for a substitute to the "Brink" separator/hydrator for the recovery of phosphoric acid. Although the "Brink" is a standard and proven equipment in a conventional thermal acid plant, its capital cost is high (54% of total capital requirement) and pressure drop is excessive, 12 in w.g. In future pilot plant work, an alternative device will be tested.

A safety study of PhoSNOX process has been conducted by FMC based on an early version of process configuration. This study indicated that potential hazards do exist, however, they can be avoided by taking proper precautions in: 1. employee safety training for P<sub>4</sub> handling, 2. fire prevention and protection procedures, 3. equipment maintenance procedures, 4. process controls and interlocks, and 5. adequate design to prevent P<sub>4</sub> from escaping. Because the PhoSNOX process was still evolving, some process features were undergoing changes or improvements for either technical or safety reasons. FMC recommended that another safety evaluation be performed when the process design is finalized.

A pilot plant testing program for the PhoSNOX process has been planned. The

objectives of the program are to verify the process performance and feasibility, and to obtain process data for scale up to commercial demonstration units.

#### References

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2. D.K. Liu, D. X. Shen, and S.G. Chang, Removal of NO<sub>x</sub> and SO<sub>2</sub> from flue gas using aqueous emulsions of yellow phosphorus and alkali, *Environ. Sci. & Technol.*, 25, 55, 1991.
3. G.C. Lee, D.X. Shen, D. Littlejohn, and S.G. Chang, The use of wet limestone systems for combined removal of SO<sub>2</sub> and NO<sub>x</sub> from flue gas, Lawrence Berkeley Laboratory report LBL-27595, also in an EPRI report, presented at the 1990 SO<sub>2</sub> Control Symposium sponsored by the US E.P.A. and the Electric Power Research Institute, May 8-11, 1990, New Orleans, Louisiana.
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5. D. Littlejohn and S.G. Chang, The solubility of the potassium salts of nitrogen-sulfur compounds, Lawrence Berkeley Laboratory Report LBL-30375, submitted to IE&C for publication, 1991.
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Table 1

#### PROCESS ECONOMIC PROJECTIONS AND COMPARISONS

Process	%NO <sub>x</sub> Reduction	P/NO <sub>x</sub>	Capital \$/kW	Levelized Cost	
				mills/kWh	\$/ton NO <sub>x</sub>
PhoSNOX <sup>(1)</sup>	90	1.0	37	6.8	2,680
	90	0.75	37	5.7	2,250
	90	0.5	37	4.6	1,800
	50	0.5	34	3.4	2,370
SCR (EPRI) <sup>(2)</sup>	80		102-125	6.8-7.6	2000-4000
Urea Injection <sup>(3)</sup>	30-60		5-15	3-4	700-3500

#### Notes

- (1) Byproduct credits are \$300/ton of P<sub>2</sub>O<sub>5</sub>
- (2) Cichanowicz, J.E. and Dene, C.E., et al, "Postcombustion NO<sub>x</sub> Controls: Potential Options for Present and Future Generation," presented at the International Symposium on Performance Improvement Retrofitting, and Repowering of Fossil Fuel Power Plants, March 6-9, 1990, Washington, D.C. Higher costs are for post-FGD selective catalytic reduction. Lower costs are for hot-side SCR. A catalyst life of 4 years for both configurations.
- (3) Eskinazi, D. and Cichanowicz, J.E., "Stationary Combustion NO<sub>x</sub> Control - A Summary of the 1989 Symposium," *APLA Journal*, Vol. 39, No. 8, August 1989, P. 1131.



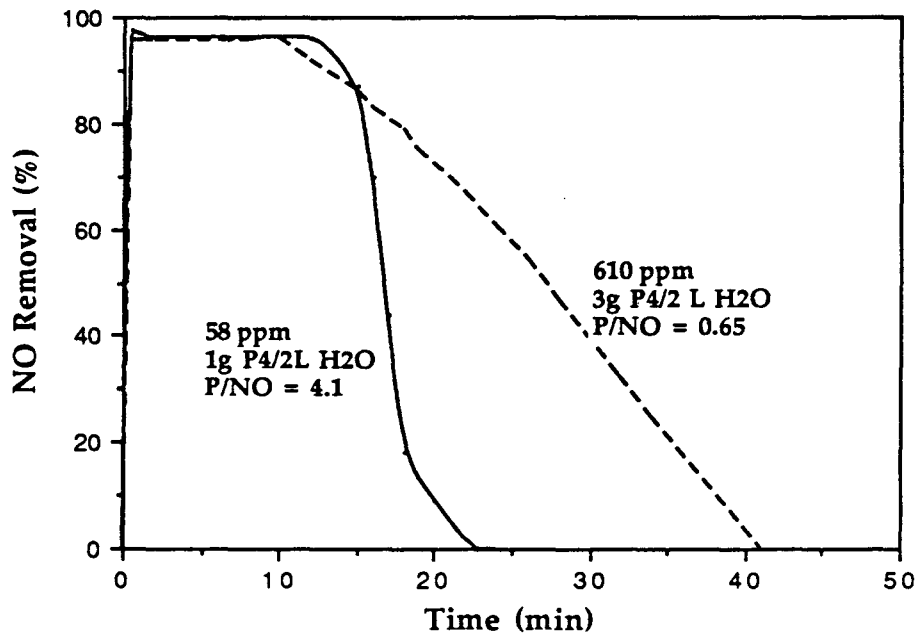


Figure 1 Removal efficiency of NO for NO concentrations of 58 and 610 ppm in the flue gas

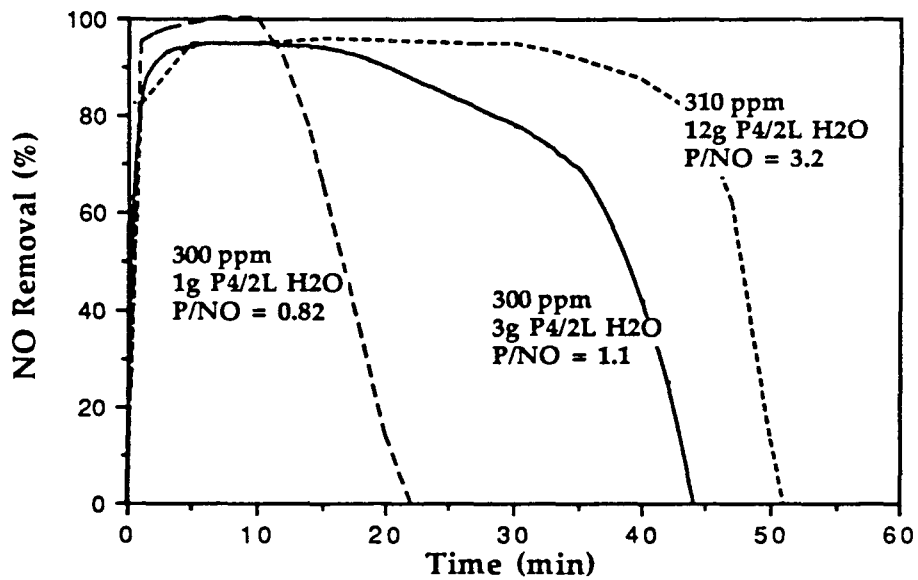


Figure 2 The dependence of stoichiometric ratio (P/NO) on the concentration of yellow phosphorus in spraying liquors

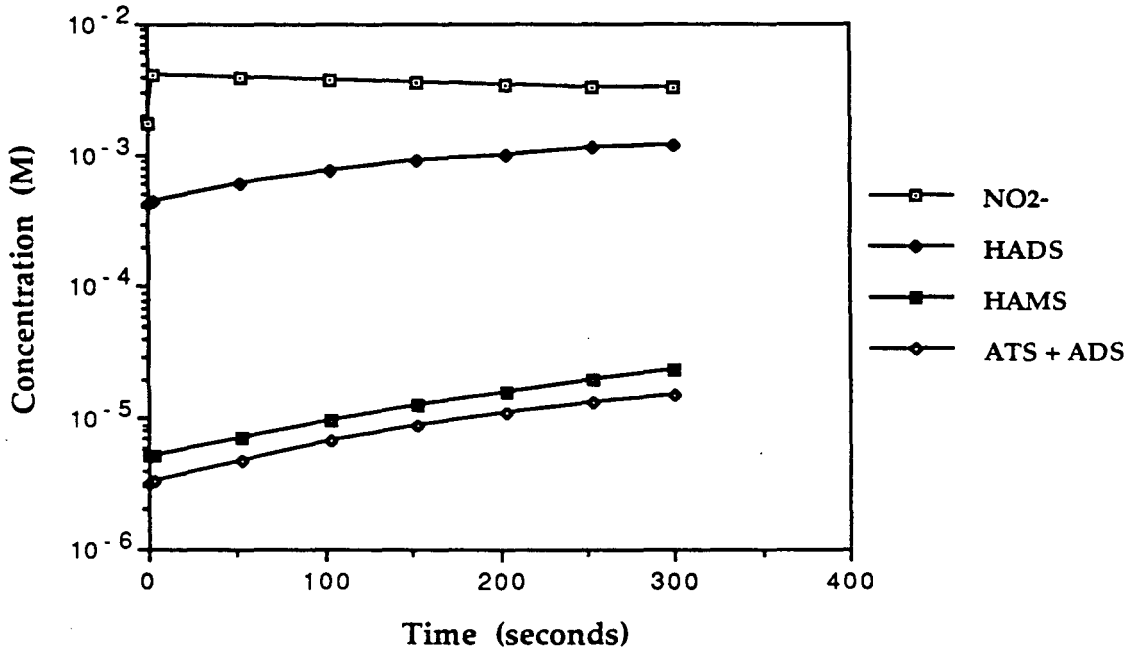


Figure 3 The concentration profiles of the nitrogen-sulfur compounds in the scrubbing liquors as a function of time

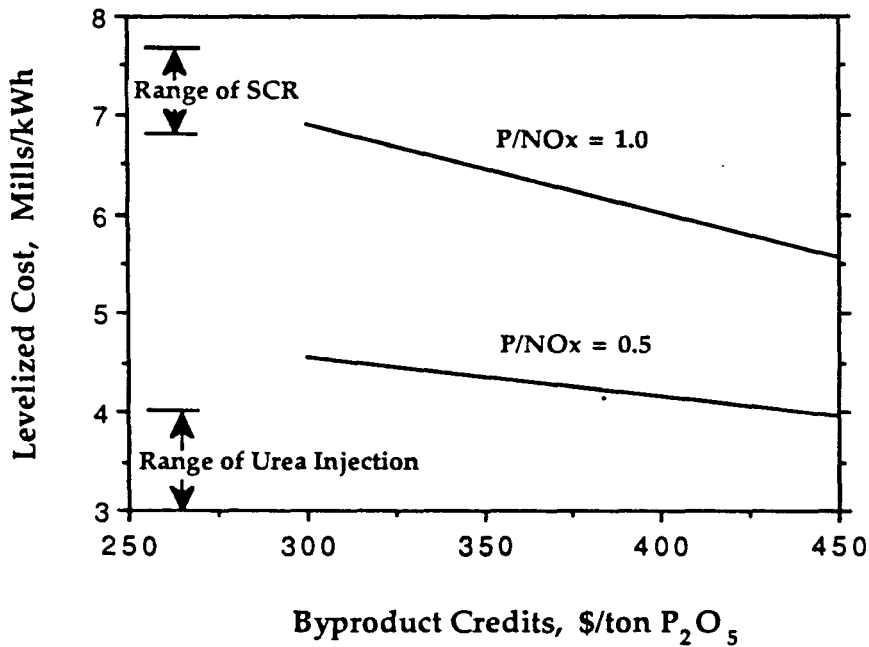


Figure 4 Effect of byproduct credits on levelized costs (Based on a 90%, 80%, and 30-60% NO<sub>x</sub> reduction in PhoSNOX, SCR, and Urea Injection respectively)

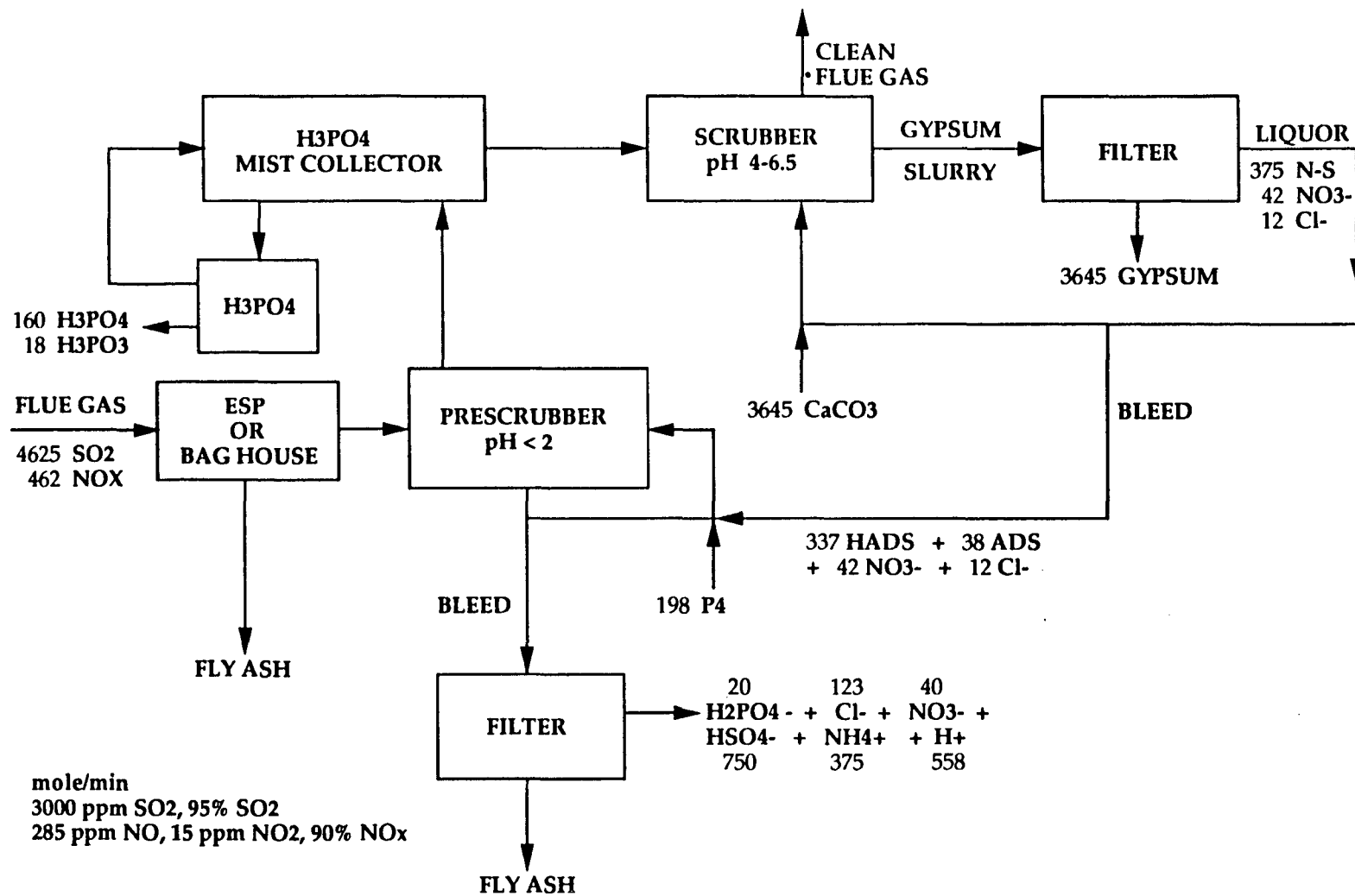


Figure 5 A Conceptual Flow Diagram of the LBL PhoSNOX Process

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