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THE USE OF WET LIMESTONE SYSTEMS FOR COMBINED REMOVAL OF SO_2 AND NO_x FROM FLUE GAS*

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ABSTRACT

A new approach by utilizing yellow phosphorus in conventional wet limestone systems for high efficiency control of SO_2 and NO_x emissions from power plants has been developed. The addition of yellow phosphorus in the system induces the production of O_3 which subsequently oxidizes NO to NO_2. The resulting NO_2 dissolves readily and can be reduced to form ammonium ions by dissolved SO_2 under appropriate conditions. Yellow phosphorus is oxidized to yield P_2O_5 which picks up water to form H_3PO_4 mists and can be collected as a valuable product.

Proof of concept experiments have been performed using a 20 acfm bench-scale system. The results show that better than 90 percent of SO_2 and NO in simulated flue gas can be removed. Stoichiometric ratios (P/NO) ranging between 0.6 and 1.5 were obtained. This ratio depends on operating conditions as well as the process configuration. A conceptual process flow diagram has been proposed. A preliminary cost evaluation of this approach appears to indicate great economic potential.

INTRODUCTION

Currently, the most widely used technology for control of SO_2 emissions from power plants has been wet limestone FGD (flue gas desulfurization) systems. The technology most often recommended to achieve high levels of NO_x control (~80% efficiency) has been SCR (Selective Catalytic Reduction). However, separate control of SO_2 and NO_x is very costly because of the combined costs for both technologies. In addition, there is very limited experience with SCR on US coal with high sulfur content and variable ash composition. High SO_2 concentration promotes the formation of ammonium sulfate/bisulfate particulates, which result in plugging of air heaters of boilers(1). Ash composition rich in arsenic and alkali could be detrimental(1) to catalysts employed in the SCR system.

The modification of a wet limestone system to allow simultaneous NO_x removal could provide a cost-effective alternative. Most of the NO_x in flue gas is NO (about 95%), which cannot be removed in a conventional limestone system because of its low solubility. One approach to avoid this problem is to oxidize NO to the more soluble NO_2. Several processes(2) have been developed based on this approach by using oxidants such as O_3 or ClO_2. Despite high removal efficiency of both SO_2 and NO_x, these processes have not been demonstrated to be cost-effective. The major reason is believed to be the high cost of these oxidants(3).

We have recently discovered a new and cost-effective method(4) for the generation of O_3 in a wet limestone system. In previous O_3-based systems, O_3 was generated by a corona discharge which would consume about 7-9% of the energy produced(3) from a power plant just to oxidize about 300-500 ppm NO in the flue gas. Our method uses chemical reactions of yellow phosphorus (P_4) with O_2 in the flue gas to produce O_3 inside a scrubbing system. The major oxidation product of P_4 is phosphoric acid which is more valuable than P_4 on a phosphorus weight basis(5).

In an earlier report(4), we have shown that aqueous mixtures of yellow phosphorus and limestone could effectively remove SO_2 and NO_x from simulated flue gas. The experiments were carried out in a 2 inch diameter bubbling absorber column with 200 ml of reaction mixture. The gas flow rate was about 3.5×10^{-2} acfm (1

liter/min), corresponding to a superficial gas velocity of 0.028 ft/sec 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 is much faster (8-12 ft/sec), and the contact time much shorter (2-5 sec). Consequently, the mass transfer and chemical reaction kinetics are less favorable under the conditions of a commercial system. In order to determine whether the P_4 additive is still effective with wet limestone systems at realistic conditions, we constructed a 20 acfm bench-scale scrubber system that simulates as close as possible the conditions of a commercial system. This paper addresses the scale-up test results. Also, a conceptual process flow diagram and a preliminary cost projection of a wet limestone system employing phosphorus additive for combined removal of SO_2 and NO_x are reported.

EXPERIMENTAL

A simulated flue gas mixture with about 5% oxygen was prepared by passing liquid nitrogen from a standard pressurized 160 liter dewar through a vaporizer column (Hex Industries) and by mixing the gas with compressed air to obtain the desired oxygen concentration. NO and SO_2 were blended in to give concentrations of 275-350 ppm and 1500-3000 ppm, respectively. CO_2 could be added up to approximately 10% of the total gas flow. The gas stream flowed, at a rate of 20 acfm, through an electric air heater where it was heated to a temperature of 350°F. The heated gas then entered the absorber. Two types of absorber were tested: a spray tower and a bubbling absorber. The spray tower absorber was a 4 in diameter by 4 ft long glass column installed with spray nozzles (Spraying Systems, Inc.).Two different spray nozzle set-ups were tested: a two nozzles (2.0 gal/min per nozzle) in series set-up and a ten nozzle (0.2 gal/ min per nozzle) set-up, in which nozzles were divided into two parallel rows with each row containing 5 nozzles in series. An aqueous mixture of P_4 and limestone slurry was sprayed in the absorber. A countercurrent flow of flue gas entered at the base of the absorber and passed upward through the falling spray of slurry(Figure 1). The bubbling absorber was a scaled-down simulation of the Bechtel CT-121 system. The bubbling absorber system included a prescrubber and a scrubber. The spray tower column just described was used as a prescrubber. The scrubber column was constructed of a 4 in diameter by 4 ft

section stainless steel pipe. Four 5/8 in diameter stainless steel tubes served as impingers directing the gas into the limestone slurry at the bottom of the column. An aqueous emulsion of P_4 was sprayed downward in a prescrubber which quenched and conditioned the flue gas flowing upward. The pretreated flue gas then entered a scrubbing column downward through impingers that submerged about 10 inches under the aqueous limestone slurry(Figure 2). A froth layer was formed when the gas entered the scrubber, which provided a greatly extended interficial area for gas-liquid contact. Air (0.85 cfm) was fed into the bottom of the scrubber to force-oxidize the HSO_3^- to SO_4^{2-}. Probes in the column allowed measurements of pH and temperature.

The concentration of P_4 in scrubbing liquors ranged from 0.5 to 0.8% w/w, while that of limestone was 6-10% w/w. A 2-liter Erlenmeyer flask was used as a hold tank for liquid mixture from the spray column. A liquid mixture was recirculated with a centrifugal pump (Price Pump Co.) to the top of the spray column. The pH of the scrubbing liquor was controlled by feeding an aqueous mixture of limestone and lime from a thermostatted reservoir (50°C) to the hold tank by a Masterflex pump (Randolph-Austin Corp.). The pH range studied was 3.5 to 6. The hold tank temperature was controlled at 50-55°C. P_4 could be continuously fed into the system from a burette containing liquid P_4 and water. P_4 (specific gravity 1.80) settled at the bottom of the burette. The burette was wrapped with a heating tape to maintain the temperature of P_4 in the burette above 44°C, its melting point.

The gas from the absorber was then directed through a washing column. In the washing column, concentrated phosphoric acid (40-60%) was sprayed through a 1 gal/min nozzle (Spraying Systems, Inc.) and recirculated by a centrifugal pump to absorb the phosphorus "white smoke". The phosphorus oxidation process generates finely divided phosphorus pentaoxides, which pick up moisture to form phosphoric acid aerosols, giving the appearance of white smoke. Therefore, recovery of the white smoke yields a valuable byproduct, phosphoric acid.

The NO_x chemiluminescent analyzer and the SO_2 fluorescent analyzer have intake connections to the gas stream at various points along the system. The NO, NO_x and SO_2 concentrations can thus be measured and the effectiveness of the absorber operation can be evaluated.

Liquids from the different columns in the system can be analyzed by ion chromatography(6) and laser Raman spectroscopy(7) to determine the identity and concentration of the anions present. The solid precipitates can be analyzed by FTIR and laser Raman spectroscopy.

RESULTS AND DISCUSSION

At a flow rate of 20 acfm, the superficial velocity of flue gas in a 4 in diameter column is about 4 ft/sec, which is typical in a CT-121 scrubber. This is slower than that in spray tower systems, where the velocity is 8-12 ft/sec. However, the gas-liquid contact time and L/G ratio are more significant physical parameters to simulate when scaling down. In the case of a spray tower scrubber, the contact time of gas and liquid sprays is about 2-5 sec and L/G ranges between 60 and 120 depending on the SO_2 concentrations and removal requirements. In the case of a CT-121 scrubber, the SO_2 removal efficiency is a function of the depth of submergence of the spargers. A submergence of 8 inches will generally provide 90% removal efficiency with a gas superficial velocity of 4 ft/sec. A 10-inch submergence was provided in the test equipment. The height of froth layer created in a 4 in column is somewhat larger than that in a commercial reactor, however. The main objective of the small bench-scale test was to prove the concept of NO_x removal simultaneously with SO_2 removal in wet limestone systems, and not to obtain data for scale-up to a commercial size.

The results of a typical run on the removal efficiency of NO and SO_2 is shown in Figure 3. This was a run using a bubbling absorber. An aqueous emulsion of P_4 initially containing 0.8% w/w P_4 was sprayed and recirculated in the prescrubber. The initial limestone concentration in the bubbling scrubber was 6% w/w and the temperature of the limestone slurry was 55°C. The flue gas contained 300 ppm NO, 1500 ppm SO_2 and 4.5% O_2. The flow rate of flue gas was 15.60 acfm, corresponding to a superficial velocity (V_f) of 3.3 ft/sec in the column. The removal efficiency of NO could be maintained at more than 85% during most of the experiment until near the end of the run, when the concentration of P_4 was substantially depleted. Also, the initial removal efficiency of NO was not as good. This is attributed to the poor mixing of P_4 with water at the beginning of the experiment. The spray nozzles

can break up P_4 globules and create a finely dispersed P_4 emulsion in water. The removal efficiency of SO_2 depends strongly on the pH of the scrubbing liquor. Initially, SO_2 was removed completely at a pH of 5.5. The efficiency dropped to about 90% when the pH of slurry decreased to 4.5.

The NO removal efficiency measures the effectiveness of NO_x absorption in the scrubbing liquor, and depends on the extent of NO oxidation to NO_2, the mixing of flue gas with liquor, and sulfite/bisulfite ion concentration.The oxidation efficiency measures the effectiveness of the oxidation of NO to NO_2 by the P_4-induced oxidation method. The NO oxidation efficiency is related to the concentration of P_4 in the spray liquor, O_2 concentration in the flue gas, temperature, and the mixing of the spray with flue gas. The factors influencing the mixing include the L/G ratio, size and uniformity of the spray, and the contact time.

The NO oxidation and removal efficiencies as a function of L/G and P_4 concentration are shown in Figures 4 and 5 for a spray tower and a bubbling scrubber, respectively. These 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 liquor. As a result, the superficial velocity and contact time of the flue gas with the spray also varied. With a spray tower absorber, an aqueous emulsion of P_4 and limestone was sprayed and recirculated in a single spray column. Therefore, the generation of O_3, the oxidation of NO to NO_2, and the absorption of NO_2 and SO_2 in scrubbing liquor took place in one column. The oxidation efficiency was more than 80% at a L/G of 60, while the removal efficiency was only 60%. The removal efficiency did not reach 80% until a L/G of 90. The increase of P_4 concentration from 0.5% to 0.8% improved slightly both the oxidation and removal efficiencies. The effect was more apparent at low L/G values. With a CT-121 scrubber, the oxidation occurred in a prescrubber where an aqueous emulsion of P_4 was sprayed, and the absorption took place in a bubbling absorber containing a limestone slurry. The oxidation efficiencies were more than 90% and the removal efficiencies more than 80% at a L/G of 60 or more. These results are better than those with a spray tower scrubber at given experimental conditions. This is attributed mainly to the difference in spray quality between two types of scrubbers. The spray nozzles are susceptible to clogging when the recirculating liquor contains limestone and

gypsum particles. The limestone in the spray may also surround the P_4 droplets and reduce the effective concentration of P_4 .

Because the diameter of the spray column is 4 in, the droplets hit the wall in a short distance after being sprayed. The liquor then flows down along 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 6 shows a plot of the NO oxidation and removal efficiencies as a function of contact time. The results were obtained with a spray tower scrubber. 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 NO oxidation achieved 100% efficiency, and the NO_x removal reached 90% efficiency with a contact time of 1.4 secs, which is less than that (2-5 secs) in a commercial system. Likewise, a plot of NO oxidation efficiency as a function of contact time in a prescrubber of a CT-121 simulation system is shown in Figure 7. The spraying liquor was composed of an aqueous emulsion of P_4 and did not contain limestone. The spray appeared to be more uniform and the nozzles did not show clogging problems. The contact distance was estimated to be 2.5 ft. The oxidation efficiency was slightly better than that in a spray tower system at the same contact time, but the improvement was less than the experimental uncertainty.

The stoichiometric ratio P/NO measures the effectiveness of P_4 utilization in the removal of NO from flue gas. In an earlier well-controlled laboratory experiment(8), the best P/NO ratio determined was 0.5. The P/NO ratios determined were in the range of 1.0-1.5 for the bench-scale spray tower, and 0.6-1.0 for the CT-121 configuration. The P/NO ratios were determined from batch runs. A known weight of P_4 was added in water, then the experiment was carried out until the NO removal reached zero. By integrating the NO removal curve for the entire period of the experiment, and knowing the amount of P_4 used, the P/NO ratio can be calculated. A P/NO determination for a constant removal efficiency of NO has not been performed. This determination would require stable and continuous operating conditions during an experiment. Gypsum separation from scrubbing liquors was difficult with the present small set-up and plugging of nozzles and

tubing made a stable spraying operation difficult to sustain sufficiently long to obtain a meaningful P/NO measurement.

An investigation of factors affecting P/NO is underway. A large amount of atomic O was detected(9) in the reaction zone during the reaction of P_4 with O_2. The reaction is believed to proceed via a branched-chain mechanism(10). Investigators(11-13) have identified several elementary reactions involved in the chain, and have determined rate constants for some of the reactions. However, a complete list of elementary reactions is not yet available. Dainton and Kimberley(14) have proposed the following reaction scheme:

$$P_4 + O_2 \longrightarrow P_4O + O \quad (1)$$

$$P_4O_n + O_2 \longrightarrow P_4O_{n+1} + O \quad (2)$$

where n = 1,2,.....9

The overall reaction is

$$P_4 + 10\,O_2 \longrightarrow P_4O_{10} + 10\,O \quad (3)$$

The reaction of O with O_2 forms O_3:

$$10\,O + 10\,O_2 + 10\,M \longrightarrow 10\,O_3 + 10\,M \quad (4)$$

According to this reaction scheme, each P_4 reacts with 10 O_2 to generate 10 O_3. If all the O_3 produced oxidizes NO to NO_2 , the P/NO ratio will be 0.4, provided the removal of NO occurs by the dissolution of NO_2(or N_2O_4). The P/NO ratio will be 0.2 if the removal of NO occurs by the dissolution of N_2O_3. In reality, the dissolution of a mixture of NO_2 and N_2O_3 in the scrubbing liquor is more likely. The O_3 generated may be consumed by reaction with SO_2 through gas phase as well as liquid phase reactions, which would increase the P/NO ratio. The gas phase reaction $SO_2 + O_3 \longrightarrow SO_3 + O_2$ is much slower (rate constant $k<8\times10^{-24}$ cm^3. $molecule^{-1}.sec^{-1}$ at 20°C)(15) than $NO + O_3 \longrightarrow NO_2 + O_2$ ($k = 1.7\times10^{-14}$ $cm^3.molecule^{-1}.\ sec^{-1}$ at 20°C)(16) and is negligible. The reaction of O_3 with HSO_3^- /SO_3^{2-} in liquid phase is fast(17), but takes place only after the dissolution of O_3 in scrubbing liquors. The solubility of O_3 is small. The Henry's constant(18) of O_3 is 1.23×10^{-2} $M.atm^{-1}$ at 20°C. The concentration of gaseous O_3 produced is related to the vapor pressure of P_4 (19), which is about 325 ppm at 50°C. (In reality, P_4 concentration is expected to be much smaller because of kinetic limitations. The

residence time of spray in a column is short. The P_4 evaporation rate from the spray is the rate determining step.) One can calculate that the concentration of O_3 dissolved in the liquor is only 4.0×10^{-5} M when in equilibrium with 3250 ppm of O_3, the upper limit in a spray column. Therefore, the dissolved O_3 is only a small fraction (less than 1%) of the total O_3 at a typical L/G ratio (60-120). Also, O_3 can be consumed by P_4 during its oxidation. The rate constants of reaction of O_3 with P_4 and its oxidation derivatives have not been reported. It is difficult to estimate the fraction of O_3 that would be consumed by phosphorus containing species. However, the reaction rate constant(12) of P_4 with O_2 is comparable to that of P_4 with O . The concentration of O_2 is orders of magnitude larger than O. Most of the P_4 is expected to be oxidized by O_2. Based on the chemistry described, the presence of SO_2 in the flue gas is probably not going to affect the result significantly. The P/NO ratio can be improved by using good mixing conditions, where the P_4 spray is dispersed uniformly and the O_3 is accessible to the NO in the flue gas. Also, the temperature, P_4 concentration of the spraying liquor, NO and O_2 concentrations in the flue gas, and L/G will influence the P/NO ratio. Furthermore, O_3 and O may be consumed on the surface of the wall. A large-diameter spray column will reduce this wall effect and improve the effectiveness of P_4 utilization.

The fate of P_4, NO, and SO_2 in the system has been studied. The reaction of P_4 with O_2 generated white smoke. The concentration of white smoke in flue gas appeared to decrease slightly as the flue gas passed through the absorber. The analysis of the scrubbing liquor by ion chromatography showed that the liquor contained phosphorus-containing species adding up to only 8-12%, and 15-25%, of the P_4 consumed with a spray tower and with a CT-121 absorber, respectively. The unabsorbed white smoke could be removed from the flue gas by treating it downstream from the absorber with concentrated (40-75%) phosphoric acid. The oxidation products of P_4 consisted of phosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3), and hypophosphorus acid (H_3PO_2), with their molar ratio roughly in 10, 2, and 0.2, respectively, at the experimental conditions employed. The factors influencing the distribution of oxidation products are under investigation. It would be desirable to produce H_3PO_4 only.

The analysis of scrubbing liquors revealed the presence of nitrogen-sulfur

compounds, in addition to NO_3^-, HSO_3^-, SO_4^{2-}, $H_2PO_4^-$, $H_2PO_3^-$, and $H_2PO_2^-$. Only 5 to 15% of the NO removed was converted to NO_3^-. The majority of NO absorbed was found to be converted to nitrogen-sulfur compounds. The nitrogen-sulfur compounds are intermediates produced from the reaction of NO_2^- with HSO_3^-.

Many concurrent and consecutive reactions(20) can take place and result in the production of intermediates, including hydroxyimidodisulfate [$HON(SO_3^-)_2$], hydroxysulfamate [$HONHSO_3^-$], hydroxylamine [NH_2OH], nitridotrisulfate [$N(SO_3^-)_3$], imidodisulfate [$HN(SO_3^-)_2$], and sulfamate [$NH_2SO_3^-$]. These nitrogen-sulfur intermediates have different reactivities and exhibit different half-lifes in the scrubbing system. The steady state concentrations of these intermediates vary depending on the scrubbing conditions. Hydroxyimidodisulfate and imidodisulfate are two intermediates most often found in high concentrations under the experimental conditions employed. When there is an excess of HSO_3^- present in the liquor, such as conditions encountered using flue gas from a high-sulfur coal, these nitrogen-sulfur compounds are converted eventually to sulfamate ion, which then hydrolyzes to produce NH_4^+ ion in an acidic medium.

$$NO_2^- + 2\,HSO_3^- \longrightarrow HON(SO_3)_2^{2-} + OH^- \quad (5)$$

$$HON(SO_3)_2^{2-} + HSO_3^- \longrightarrow N(SO_3)_3^{3-} + H_2O \quad (6)$$

$$N(SO_3)_3^{3-} + H_2O \longrightarrow HN(SO_3)_2^{2-} + SO_4^{2-} + H^+ \quad (7)$$

$$HN(SO_3)_2^{2-} + H_2O \longrightarrow H_2NSO_3^- + SO_4^{2-} + H^+ \quad (8)$$

$$H_2NSO_3^+ + H^+ \longrightarrow H_2NSO_3H \quad (9)$$

$$H_2NSO_3H + H_2O \longrightarrow NH_4^+ + SO_4^+ + H^+ \quad (10)$$

The overall reaction is

$$NO_2^- + 3\,HSO_3^- + H_2O \longrightarrow NH_4^+ + 3\,SO_4^{2-} + H^+ \quad (11)$$

A fraction of the absorbed SO_2 is converted to nitrogen-sulfur intermediates as described above. These intermediates will eventually decompose to form SO_4^{2-} as the final product of absorbed SO_2.

PROCESS ECONOMIC PROJECTIONS

The following process economic projections are pre-pilot plant estimates and are very preliminary. They are presented at this stage of development only to indicate whether or not further process development work is justified, and we think it is. After the completion of further pilot plant testing, the process configuration will be better defined and a more realistic economic projection will be made.

Based upon a conceptual process configuration with the following features(Figure 8):

- injecting a phosphorus emulsion into an existing wet limestone scrubbing system
- adding a "Brink" separator/hydrator downstream of the scrubber to capture and convert the P_2O_5 to phosphoric acid byproduct
- installing necessary equipment to recover other byproducts (calcium phosphate and ammonium phosphate)
- adding new fan capacity to compensate for the additional pressure drop

The capital requirement would be in the range of $20-25/KW. This is about 1/4 of the estimated capital requirement for a selective catalytic reduction(SCR) system ($78-101/KW), reported in an EPRI-sponsored study in 1989(21).

As for the levelized busbar cost (for 90 percent NO_x removal), it would be in the range of 2-9 mills/kWh. The lower figure corresponds to taking full credit for all the byproducts at current listed prices. The higher figure corresponds to taking no byproduct credit at all. Realistically, one should be able to sell the byproduct acid for $300/ton which is below the thermal grade (high purity) acid price of $460/ton

or the agricultural grade (low purity) acid price of $310/ton. With a credit of $300/ton of acid, the levelized cost would be about 5 mills/kWh which compares favorably with that of a SCR system, ranged from 4 to 9 mills/kWh for up to 80 percent NO_x removal(22).

The operating cost of this process is sensitive to the P/NO ratio used, the NO_x removal requirement, and the byproduct credit (therefore market penetration). The aforementioned levelized costs are based upon a P/NO ratio of 1.0 for 90 percent NO_x removal. The best P/NO ratio achievable ,theoretically, is only 0.2-0.4 mole of P per mole of NO removed. The difference between 1.0 and 0.2-0.4 indicates there is room for improvement. The actual P/NO requirement depends on the equipment (i.e. scrubber) used for contacting the gas and the phosphorus emulsion. In the bench-scale equipment used where the contacting time was short and the mixing was relatively inefficient, the required P/NO ratio was from 0.6 to 1.0. For more efficient contacting devices and longer contact time, as typically in most commercial scrubbers, a ratio around 0.5 can be reasonably expected. Assuming the P/NO ratio can be reduced to 0.5, the levelized cost would be reduced to 5.4 mills/kWh without by-product credit, or 3.5 mills/kWh with acid credit of $300/ton. These costs compare more favorably with that of a SCR system. In future work our effort will be directed to lowering the P/NO ratio sufficiently so that the process economics become less dependent on byproduct credit and still look attractive compared to the SCR process.

Now, let us look at the phosphoric acid market perspective. For a 500 MW installation of this process, there would be approximately 8,000 tons of acid produced per year on a P_2O_5 basis. This quantity represents only 0.07 percent of the current agricutural acid market, or 0.8 percent of the high purity acid market. If 50 systems of this size (25,000 MW total) are installed, it would have to capture 3.5 percent of the agricutural acid market, which is probably not difficult to do. On the other hand, it would have to displace 40 percent of the high purity acid market, which would be difficult if not impossible. This means that the byproduct acid can compete with the high grade acid only to a limited extent, and by and large it has to compete with the low grade agricultural acid. For this reason, an average of $300/ton credit appears to be realistic. We are exploring a cooperative program with

the phosphate industry what we call a "phosphorus passing through" concept. In this concept,the phosphorus manufacturers ship the phosphorus to the power plants (the process users) then take back and market the phosphoric acid with some kind of cost adjustment or service charge. In this arrangement, the phosphorus manufacturers do not have to convert the phosphorus to acid as they normally do. The process owners or users do not have to market the byproduct. This would not alter significantly the acid supply and demand situation, and should be mutually beneficial.

To further improve the process economics, we are looking for a substitute for 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.C. In future pilot plant work, an alternative device will be tested.

In summary, pre-pilot plant economic projections for this process have been made based upon a preliminary conceptual process configuration. Further pilot plant testing in the future may contribute to process and economic improvement. A comparison of the current economic projections with those of other NO_x control technologies is given in Table 1.

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Table 1
Comparison of Process Economic Projections

Process	NO_x Control,%	Capital, $/KW	Levelized Cost,mills/kWh
Phosphorus	90	20-25	2-9(A)
			5-9(B)
			3.5-5.4(C)
SCR, in U.S.	80	78-101(21)	4-9(22)
in Europe	80	60-180(22)	
Urea Injection	30-50	5-15(22)	3-4(22)

Notes: (A) Lower figure assumes full credit for all the byproducts at current list prices, higher figure assumes no byproduct credit, P/NO = 1.0, 75% P_2O_5 recovery.

(B) Lower figure assumes $300/ton of acid credit, higher figure assumes no byproduct credit, P/NO = 1.0, 75% P_2O_5 recovery.

(C) Same as (B), P/NO = 0.5

FIGURE CAPTIONS

Figure 1. A schematic diagram of a 20 acfm bench-scale wet phosphorus/limestone process using a spray tower scrubber.

Figure 2. A schematic diagram of a bench-scale Bechtel CT-121 scrubber consisting of a spray tower prescrubber and a bubbling absorber.

Figure 3. The removal efficiency of NO and SO_2 using a CT-121 scrubber. The P/NO ratio determined for this run was 0.73.

Figure 4. The oxidation and removal efficiencies of NO as a function of L/G using a spray tower scrubber. The simulated flue gas contains 310 ppm NO, 2000 ppm SO_2, and 5% O_2.

Figure 5. The oxidation and removal efficiencies of NO as a function of L/G using a prescrubber. The simulated flue gas contains 310 ppm NO, 2000 ppm SO_2, and 5% O_2.

Figure 6. The oxidation and removal efficiencies of NO as a function of contact time of flue gas with the spray of phosphorus and limestone aqueous mixture in a spray tower scrubber.

Figure 7. The oxidation efficiency of NO as a function of contact time of flue gas with the spray of phosphorus aqueous emulsions in a prescrubber of a CT-121 system.

Figure 8. A conceptual flow diagram of a wet phosphorus/limestone process for combined removal of SO_2 and NO_x.

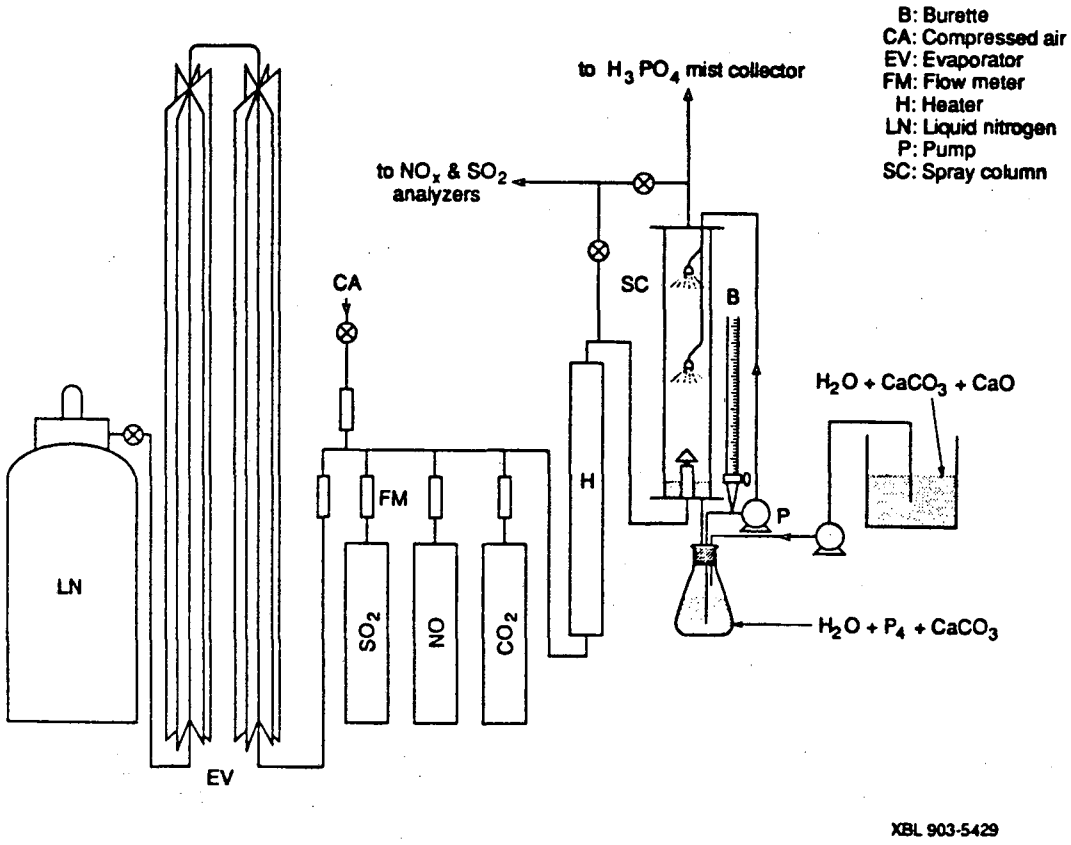
B: Burette
CA: Compressed air
EV: Evaporator
FM: Flow meter
H: Heater
LN: Liquid nitrogen
P: Pump
SC: Spray column
to H_3PO_4 mist collector
to NO_x & SO_2 analyzers
CA
SC
B
$H_2O + CaCO_3 + CaO$
H
FM
P
LN
SO_2
NO
CO_2
$H_2O + P_4 + CaCO_3$
EV
XBL 903-5429

Figure 1.

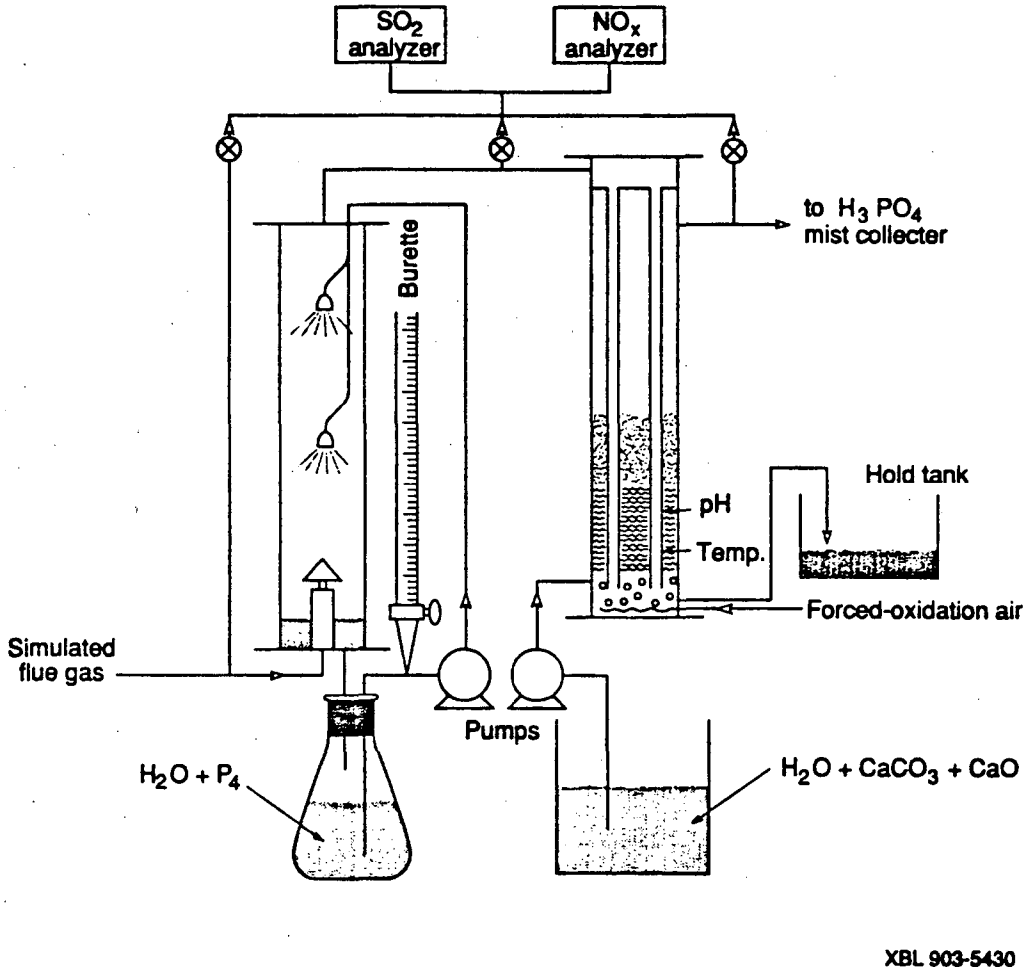
SO_2 analyzer
NO_x analyzer
to H_3PO_4 mist collecter
Burette
Hold tank
pH
Temp.
Forced-oxidation air
Simulated flue gas
Pumps
$H_2O + P_4$
$H_2O + CaCO_3 + CaO$
XBL 903-5430

Figure 2.

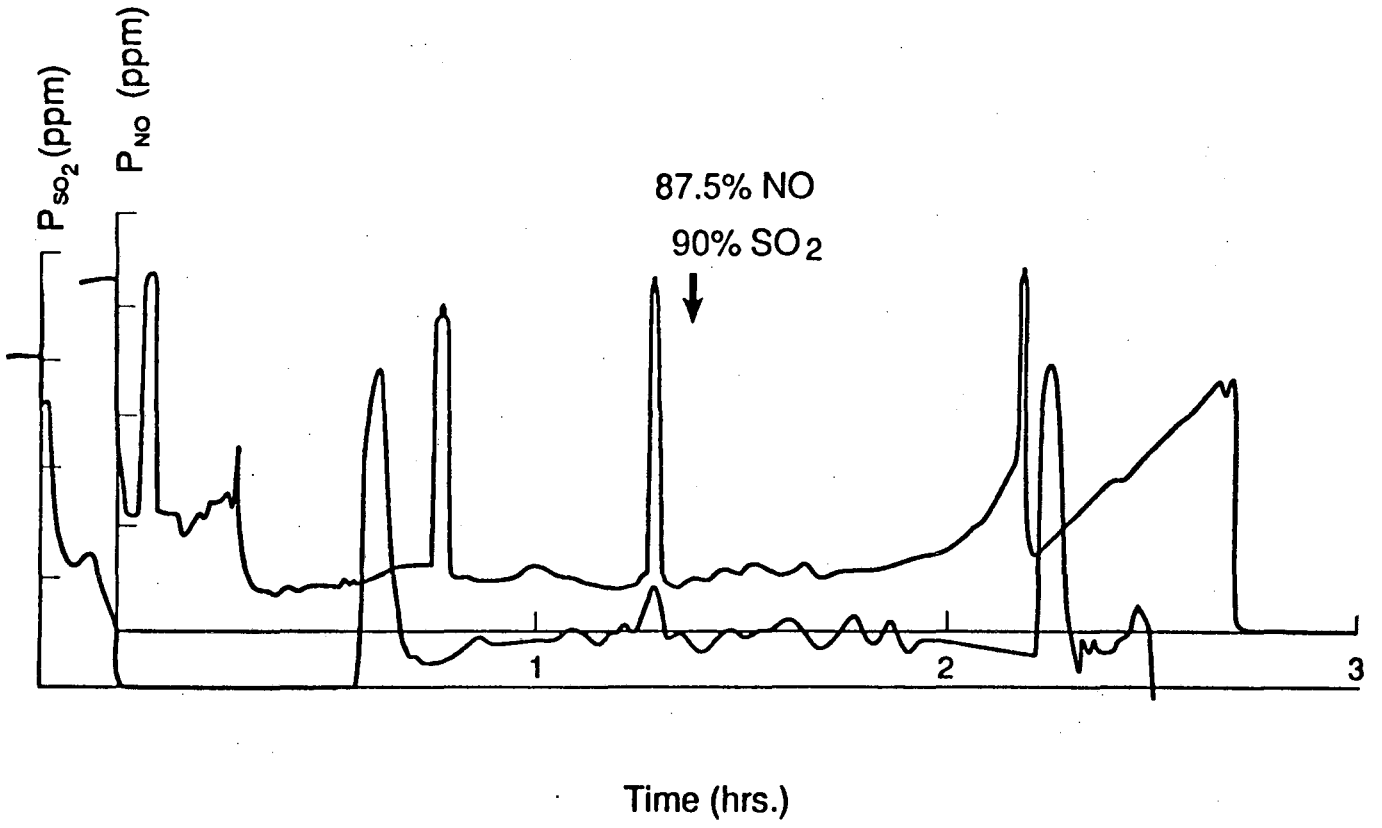

Figure 3.

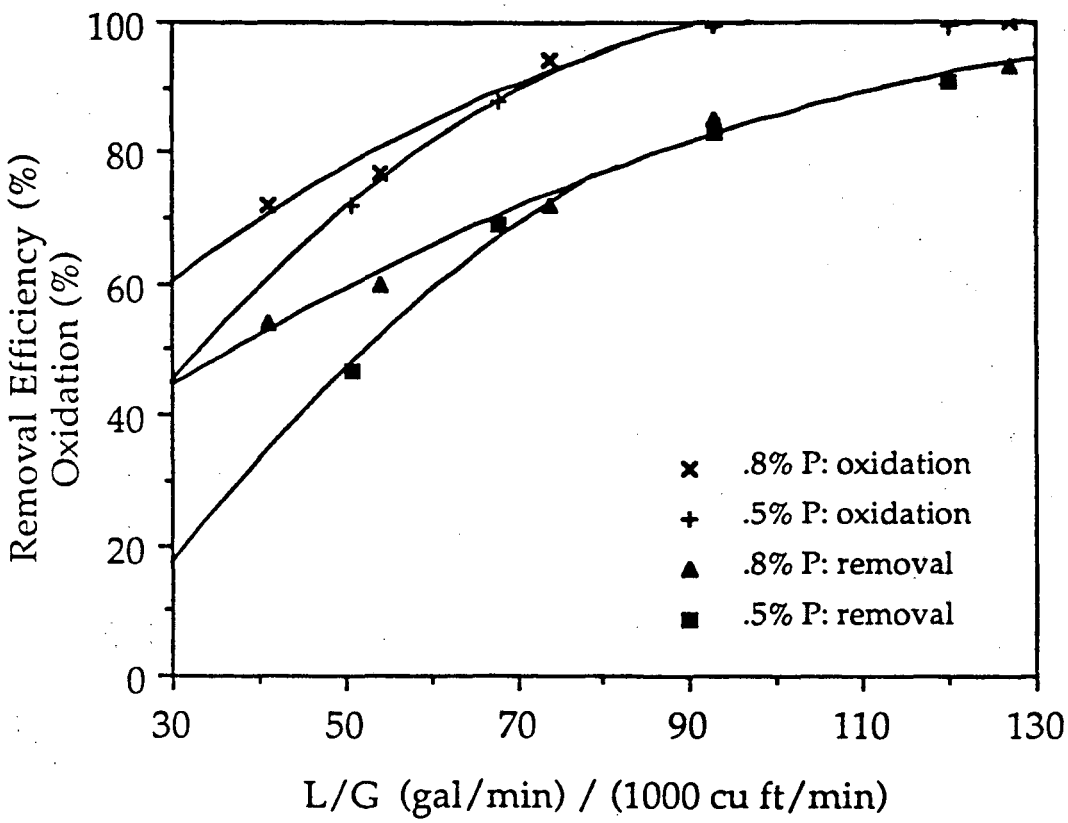
100
80
60
40
20
0
Removal Efficiency (%)
Oxidation (%)
30
50
70
90
110
130
L/G (gal/min) / (1000 cu ft/min)
.8% P: oxidation
.5% P: oxidation
.8% P: removal
.5% P: removal

Figure 4.

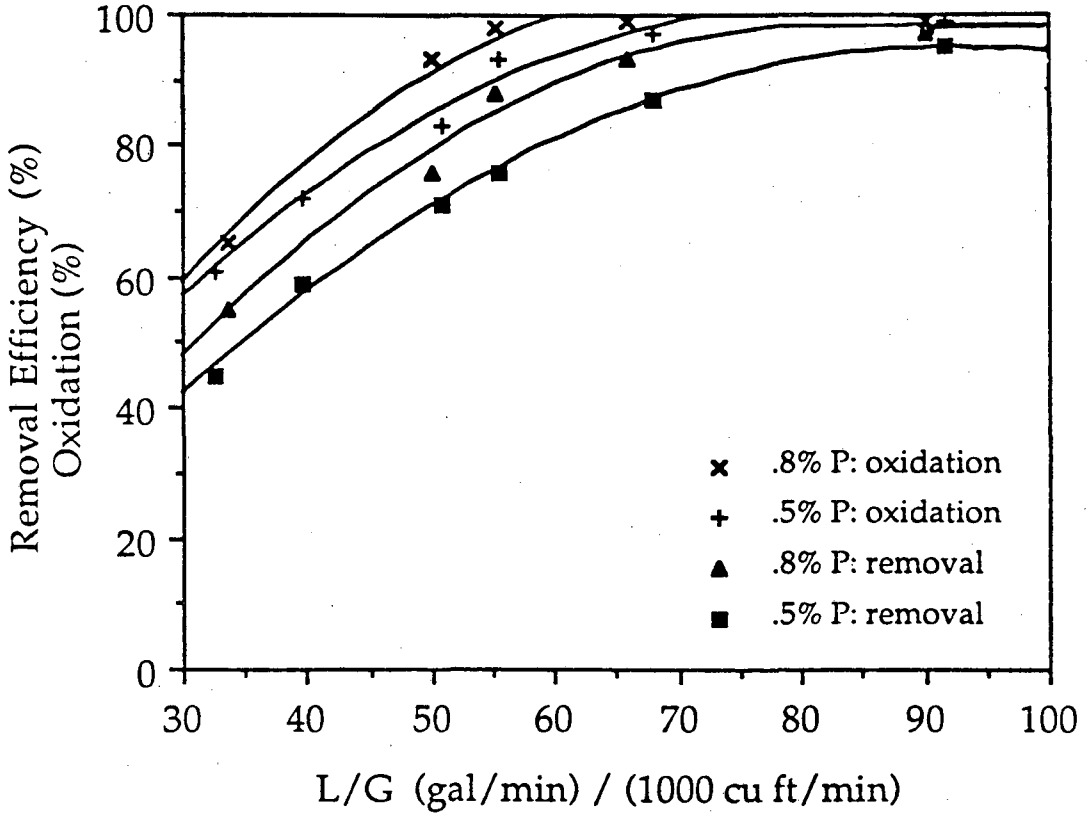
100
80
60
40
20
0
30
40
50
60
70
80
90
100
Removal Efficiency (%)
Oxidation (%)
L/G (gal/min) / (1000 cu ft/min)
.8% P: oxidation
.5% P: oxidation
.8% P: removal
.5% P: removal

Figure 5.

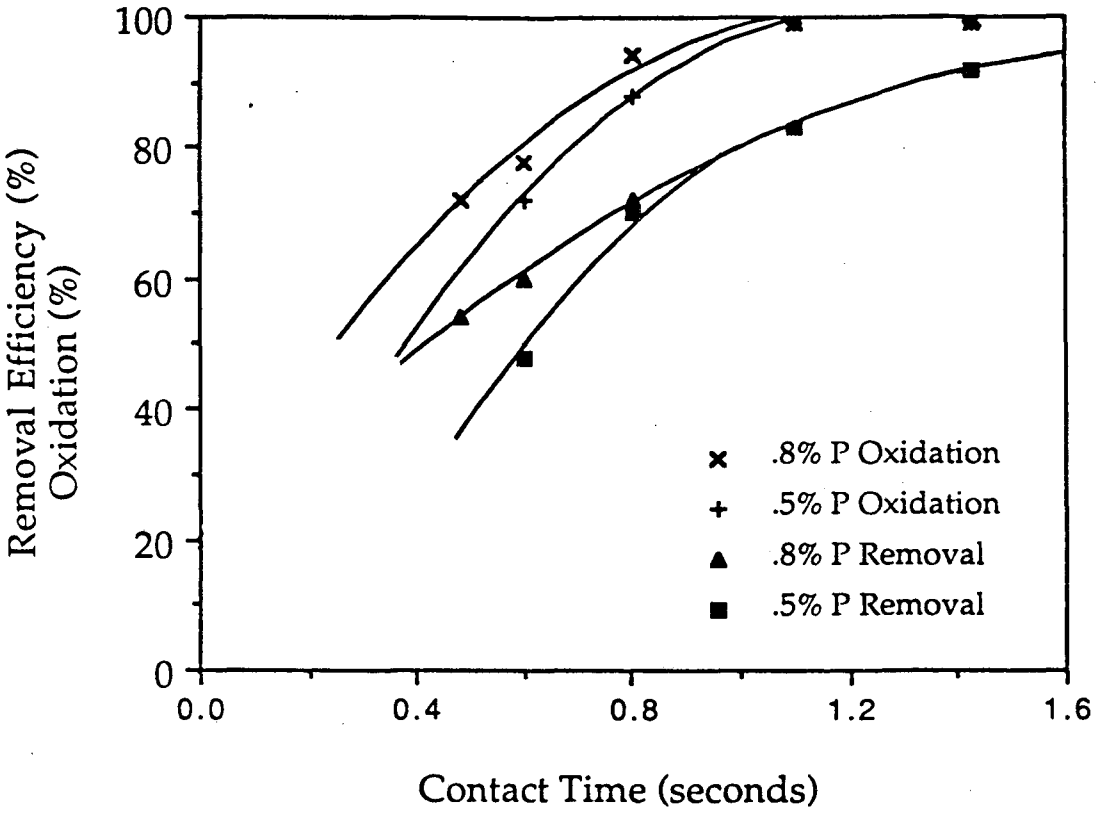
100
80
60
40
20
0
0.0
0.4
0.8
1.2
1.6
Removal Efficiency (%)
Oxidation (%)
Contact Time (seconds)
.8% P Oxidation
.5% P Oxidation
.8% P Removal
.5% P Removal

Figure 6.

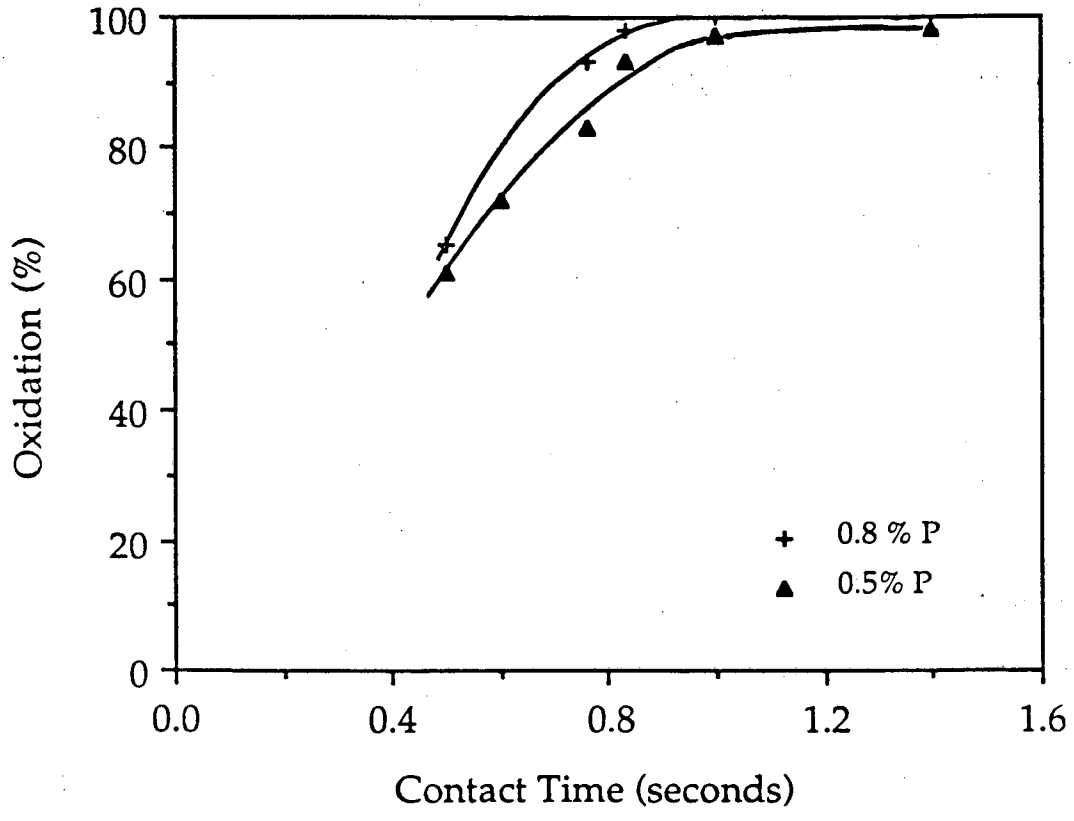
100
80
60
40
20
0
Oxidation (%)
0.0
0.4
0.8
1.2
1.6
Contact Time (seconds)
0.8 % P
0.5% P

Figure 7.

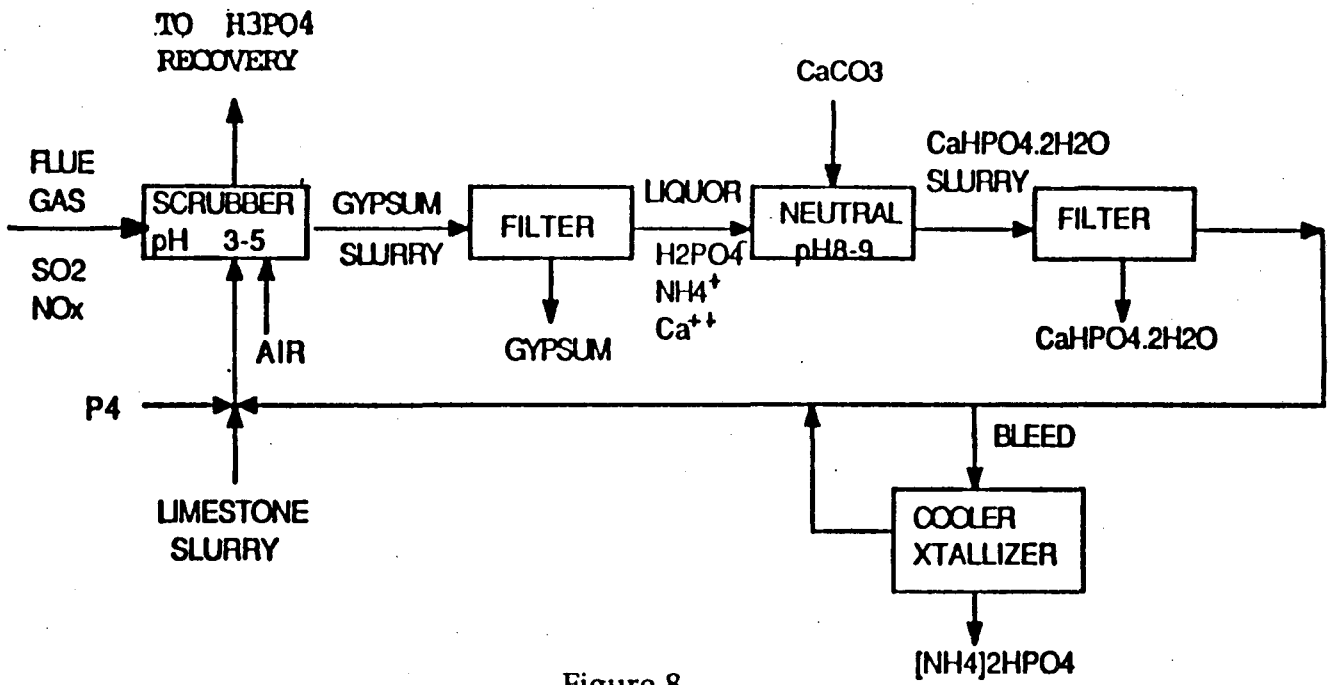
TO H3PO4
RECOVERY
FLUE
GAS
SO2
NOx
SCRUBBER
pH 3-5
AIR
P4
LIMESTONE
SLURRY
GYPSUM
SLURRY
FILTER
GYPSUM
LIQUOR
H2PO4
NH4+
Ca++
CaCO3
NEUTRAL
pH8-9
CaHPO4.2H2O
SLURRY
FILTER
CaHPO4.2H2O
BLEED
COOLER
XTALLIZER
[NH4]2HPO4

Figure 8.

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