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OPPORTUNITIES FOR INTEGRATED POLLUTION CONTROL RETROFITS

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ABSTRACT

Conventional flue gas cleanup technologies have been used for many years at electric utility and large industrial boiler sites for control of sulfur dioxide (SO_2) and particulate matter (PM). Nitrogen oxides (NO_x) control at the mandated U.S. emission levels has generally been met through combustion modification techniques. Pending legislation is expected to require the retrofit of many additional U.S. installations with SO_2 controls and may also require greater reduction of NO_x emissions.

Previous experience has shown that the best approach for control of multiple pollutants is through a single, integrated system. Integrated systems generally offer lower costs than several separate technologies, give better operability and availability of the power system, consume fewer resources (including energy), and produce less waste for disposal. Achieving integrated control is inherently difficult in a retrofit situation, particularly when some emission control systems are already in place. Several research efforts have recently been directed at this objective with a primary emphasis on combining NO_x and SO_2 control. This paper reviews both integrated wet and dry scrubbing technologies that have undergone research and development efforts and that are particularly applicable to retrofits. The discussion will focus on their performance potential and developmental status. Particulate control devices are also considered since they can contribute significantly to NO_x/SO_2 removal.

INTRODUCTION

Increased control of sulfur dioxide has been the focus of air pollution and acid deposition debates for many years, and new legislation under discussion in Congress is expected to require control of this pollutant at many more installations. Calls for greater control of nitrogen oxides have also been heard in response to their implication in environmental damage and possible links to global climate effects. This has already led to more stringent NO_x emission regulations in several countries and some parts of the United States.

While a number of options are available to remove either NO_x or SO_2 from flue gas, integrated technologies that can simultaneously remove both species (and perhaps particulate matter as well) in a single system may offer significant advantages. The benefits of such integration generally include better system operability, higher reliability, and lower capital and operating costs. In addition, there may be advantages due to lower consumption of resources, reduced waste volumes, and beneficial synergisms between the pollutants.

The construction of complete, integrated systems will be of interest for new utility plants and industrial installations, as well as existing sites that currently have minimal pollution control. However, opportunities to incorporate integrated pollution control into existing flue gas cleanup systems will be particularly important if control requirements are tightened and operators with existing SO_2 scrubbing systems are faced with the need to add additional control of NO_x. This paper describes recent research that could lead to relatively low-cost NO_x control retrofits of two of the most common flue gas desulfurization (FGD) systems: wet scrubbing and spray drying.

The dominant type of FGD in the U.S. today is wet scrubbing based on either limestone or lime. Lime scrubbing is similar to limestone processes except that the feed slurry is prepared by slaking lime rather than by grinding limestone. A basic flow sheet for a lime-based system is shown in Figure 1. High (over 90%) SO_2 removals are easier to obtain with lime than with limestone and more complete sorbent utilization is realized, but the higher cost of the raw sorbent offsets some of the advantages. The sorbent slurry is recirculated between an absorber (typically a spray tower) and a hold tank where fresh sorbent is added, and a bleed stream of reaction products is pumped to the waste disposal system or settling pond. The outlet gas from the scrubber passes through a slurry entrainment separator ("demister") and is reheated for buoyancy before discharge to the stack. The reaction products from the first generation of installed scrubbers form a $CaSO_3/CaSO_4$ sludge that is difficult to dewater, although fixation techniques involving fly ash and/or proprietary additives have been developed to give the waste stability. Second generation scrubbers have greatly reduced this problem by operating in either an inhibited or forced oxidation mode. The inhibited oxidation mode of operation uses colloidal sulfur to retard calcium sulfite oxidation resulting in larger product crystals, which improves dewatering of the product. In the forced oxidation mode, the calcium sulfite is oxidized to produce calcium sulfate (gypsum), which can be dewatered and landfilled or, in some cases, sold as a by-product.

Sodium-based systems use a scrubbing solution that avoids many of the operational problems that have hampered lime/limestone scrubbers, particularly erosion and scaling. Sulfur dioxide removals well over 90% are easily achieved. Typically, sodium carbonate is dissolved in a mixing tank and pumped to the absorber vessel. A bleed stream of scrubber effluent removes reaction products such as sodium sulfite and sodium bisulfite. This stream is sent to an evaporation pond for disposal. Due to the soluble nature of the products, groundwater contamination may be a concern.

An important variation on sodium scrubbing is the double-alkali process. It combines the high removals and good operability of the sodium process with the waste disposal characteristics of a lime/limestone scrubber. In this case, the bleed stream is pumped to a reactor tank where it is blended with slaked lime or finely ground limestone. Calcium sulfite and sulfate crystals are formed and removed for disposal while the sodium sulfite scrubbing liquor is regenerated.

Dry scrubbing technology was developed in the 1970s based on the spray drying of an alkali sorbent, typically lime slurry. The reagent slurry is pumped to a spray dryer vessel where it is atomized to a cloud of fine droplets and mixed with the hot flue gas. Virtually all of the water is evaporated by the heat of the flue gas, while SO_2 is simultaneously absorbed and reacted with the alkali.

The resulting dry powder and fly ash are collected in either a baghouse or an electrostatic precipitator and typically sent to a landfill for disposal. In some systems, a portion of the waste is recycled to the feed slurry to improve overall reagent utilization. The spray dryer outlet temperature is maintained safely above the adiabatic saturation temperature (i.e., 20-30°F higher) by controlling the water content of the slurry, and the stack SO_2 emissions are controlled by the addition of fresh lime to the slurry tank.

Spray dryer FGD systems received rapid acceptance by the electric utilities and other industries for use with low-sulfur coal. Experience at a number of facilities has established that spray drying technology is both technically and economically viable for boilers firing medium- to high-sulfur coal [1,2]. Sulfur dioxide removal rates of over 70% can be achieved in the spray dryer. With the addition of a particulate collection device yielding additional area for gas-sorbent contact, better than 90% removal can be achieved for high-sulfur coal, thereby integrating SO_2 and PM control.

The integration of NO_x control into either wet or dry scrubbers presents a considerably greater challenge. The concentration of NO_x produced in combustion varies considerably with fuel, combustor type, and specific operating conditions. For coal firing, NO_x values typically fall between 200 and 1000 ppm, while SO_2 levels for high-sulfur coal are closer to 3000 ppm. Despite the lower concentrations, nearly all of the NO_x is present in the form of nitric oxide (NO), which is much less soluble than SO_2 and therefore more difficult to scrub. Thus, conventional FGD systems absorb at most a few ppm of NO_x and do not represent a viable NO_x control strategy. Installation of a separate NO_x removal system into an existing plant is usually difficult due to limited plot space and poor retrofit accessibility. Integration of NO_x removal capabilities into existing SO_2 control processes, however, could avoid many of these retrofit difficulties, simplify the total NO_x/SO_2 control system, and also take advantage of the many scrubbers already in place.

INTEGRATED WET SCRUBBING SYSTEM

One approach to achieving integrated control in a wet scrubbing FGD system is the use of an additive to the scrubber liquor, which quickly removes any absorbed NO from solution in order to maximize the absorption driving force. One of the most widely studied additives is ferrous iron combined with the chelating agent ethylenediaminetetraacetic acid to form Fe(II)·EDTA, which combines reversibly with NO to form a ferrous nitrosyl complex. A substantial body of literature exists dealing with the use of this additive for denitrification. However, most of that work did not address combined NO_x/SO_2 control, and thereby overlooked an important synergism between NO and SO_2 in which the coordinated NO reacts with a sulfite ion, freeing the ferrous chelate for further reactions with NO [3]. This mechanism and the chemistry of other metal chelates with the potential for NO_x control have been studied extensively at Lawrence Berkeley Laboratory in a research program sponsored by the U.S. Department of Energy (DOE).

Argonne National Laboratory (ANL) has investigated the performance of several metal chelates in a laboratory-scale scrubber using four different FGD chemistries and flue gas typical of medium- to high-sulfur coal. Nitrogen oxides removals of 70% or more were obtained in a flooded-column scrubber with a sodium-based chemistry. This promising performance led to the development of a preliminary NO_x/SO_2 process concept and the granting of a U.S. patent for the preparation and application of the additives [4].

A critical problem with ferrous chelates for NO_x control is that oxygen (O_2) in the flue gas environment gradually converts the iron to the ferric state, in which it is inactive for NO_x removal. As that happens, the additive must either be replaced or regenerated in some manner. Argonne developed improved additive preparation procedures that enhanced additive stability, but oxidation remains a key issue in process development. This is illustrated in Figure 2, which shows NO_x removal performance in ANL tests with Fe(II)·EDTA at 0% and 2.7% O_2. Several approaches to resolving this issue are under investigation. Work at ANL with "secondary" additives, such as pyrogallol, that inhibit oxidation and also act as reducing agents has significantly improved additive lifetime, as shown in Figure 3. Note that the data in Figure 3 were taken with a different type of scrubber from that in Figure 2, resulting in less gas-liquid contact and slower inherent oxidation. Further work is needed to determine if this approach is economically viable.

Another approach utilizes bisulfite ions normally occurring in the scrubber liquor as reducing agents for the ferric ions. This technique has been incorporated in a process concept under development at the Pittsburgh Energy Technology Center (PETC) [5]. Elevated temperatures on the order of 70-100°C and residence times on the order of 3 h are required. Although small-scale tests have been conducted, considerable process development is still required for scaleup of this technique.

A third approach, being developed by the Dow Chemical Company, utilizes the reducing capabilities of an electrochemical cell to control additive oxidation. Field tests on a 12,000 acfm flue gas stream gave up to 70% NO removal using a packed tower scrubber and more than 90% of the iron was maintained in the ferrous state by the electrochemical cell [6].

Other development work is seeking improved chelating agents for the iron. The objective is to find combinations that offer either improved NO_x removals or greater oxidation stability (or both). For example, Argonne has used a "disk and donut" laboratory scrubber that closely simulates the mass transfer characteristics of commercial systems to compare Fe(II)·EDTA and Fe(II)·Cysteine in a sodium-based scrubber chemistry. Under operating conditions that gave 90% SO_2 removal, NO_x removals were between 25 and 40% for both additives, with EDTA giving somewhat better removal and cysteine giving better stability, as shown in Figure 4. Further long-term tests and detailed evaluation of waste handling issues are required before the preferred additive can be identified. Note that higher NO_x removals can be attained at the expense of more vigorous gas-liquid contacting (and hence greater pressure drop and energy consumption). In the extreme, removals of 70% or more for NO_x are achievable together with SO_2 removals approaching 100%.

Processing and disposal of the scrubber waste containing -- in addition to the normal SO_2 reaction products -- nitrites/nitrates, a variety of nitrogen-sulfur compounds, and perhaps other species is a second major issue for development of this technology. Pilot-scale tests of metal chelates planned by the Dravo Lime

Company [7], together with further laboratory research, are expected to resolve this issue.

INTEGRATED DRY SCRUBBING SYSTEM

To integrate NO_x removal with the SO_2/PM control capability of spray dryer systems, DOE has directed a program investigating chemical additives and modified process conditions. This research was spurred by initial data from Niro Atomizer on simultaneous NO_x/SO_2 control in a lime-based spray dryer using sodium hydroxide (NaOH) as an additive [8]. Concern arose, however, from reports of brown plume formation (resulting from low levels, 40 to 70 ppm, of nitrogen dioxide present in the stack gas) at a western utility operating a spray dryer system using a sodium-based reagent. Therefore, nitrogen dioxide (NO_2) concentration levels were monitored throughout the test program.

Although many laboratory studies have been conducted on different sorbents and additives, sodium hydroxide addition to lime slurry has undergone extensive research from small- and pilot-scale testing at PETC to industrial-scale spray dryer testing at ANL. Parametric experiments conducted in a small-scale (31-in.-diameter) spray dryer facility using lime slurry with 10 wt% NaOH addition [9] showed that spray dryer outlet temperature was the most important operating variable for both SO_2 and NO_x removal, as well as for NO_2 stack concentration changes. Increases in the spray dryer outlet temperature resulted in a rise in the NO_x removal accompanied by an increase in the NO_2 stack gas concentration, whereas SO_2 removal was observed to decrease.

In pilot-scale (0.75-MWe) spray dryer tests at PETC with 5 wt% NaOH addition [10], SO_2 removals were found to improve significantly when sodium hydroxide was added to the lime slurry feed at the elevated spray dryer outlet temperatures. Thus, although some SO_2 removal capability was sacrificed during the operation at the higher spray dryer outlet temperatures required for NO_x removal, this negative effect was partially offset by the increased absorption resulting from the presence of sodium hydroxide.

Full-scale demonstration (20-MWe) tests were conducted in the ANL spray dryer/fabric filter system in 1986 and 1988. Figure 5 is a process flow diagram of the FGD system [11]. The boiler is fired with Illinois Basin coal, nominally containing 3.5% sulfur. A 35 wt% slurry consisting of a blend of recycled solids and fresh milk of lime is pumped to the slurry feed tank. The spray dryer is 25 ft in diameter with a single rotary atomizer. Dual gas inlets are used with about 60% of the flue gas entering downward through a roof gas disperser and the remainder of gas entering upward through a central disperser. Depending upon the gas flow rate, about one-fourth to one-third of the powder produced falls to the bottom of the spray dryer and is removed by a conveyor. The remainder is entrained in the gas stream and is carried to the baghouse. The fabric filter baghouse is a four-compartment pulse-jet system containing woven fiberglass bags. Cleaning is performed off-line for one compartment at a time and is initiated when a pressure differential of about 3.5 in. H_2O is reached.

In the two field tests [10,11,12,13], sulfur dioxide removals were controlled to levels of about 70% in order to maintain compliance with the ANL operating permit. Inlet NO_x concentrations varied between 250 and 380 ppm, and inlet SO_2

levels ranged from 1500 to 2000 ppm. The only exception was during a period when SO_2 inlet levels decreased to a value of 400 ppm while low-sulfur (1% S) eastern coal was fired in the boiler.

As part of the test program, the outlet temperature from the spray dryer was gradually increased from 150°F to 210°F prior to sodium hydroxide addition. This minimized the risk of major system upsets and provided data needed to separate temperature effects from those due to the additive. Results on SO_2 removal were consistent with the known tradeoff between Ca/S stoichiometric ratio and SO_2 removal. At a spray dryer outlet temperature of 155-160°F, about 70% of the SO_2 entering the system was removed at an internal equivalence ratio[1] of about 1.0-1.05. As the outlet temperature was increased to 200°F, the internal equivalence ratio was found to increase to about 1.6-1.7 for comparable SO_2 removal. With respect to NO_x removal, no significant removal was observed under normal spray dryer operating conditions. However, at about 182°F, a dramatic transition was encountered with a very rapid increase in NO removal (up to 15%). Total NO_x removal also increased, although the rate of increase slowed considerably above 190°F. A net production of NO_2 accompanied the NO_x removal, ranging from 6 to 18 ppm. The NO_2 production appeared to take place in the baghouse, as did the increased NO removal. The sharp increase in the NO_x removal was confirmed by a strong increase in the nitrates content of the spent powder.

Sodium hydroxide was added to the lime slurry at 2.5, 5, and 10 wt% levels; weight percent was based on the rate of lime (as $Ca(OH)_2$) addition. The addition of NaOH reduced the equivalence ratio required for a given level of SO_2 control. As shown in Figure 6, adding NaOH to the lime slurry resulted in increased NO_x removal from the flue gas, with the effect being most evident at high temperature (200°F). Very little improvement in NO_x removal was found as the NaOH addition rate increased, indicating that temperature clearly had a much stronger effect on NO_x removal than the rate of addition. Thus, significant NO_x removal enhancement is possible at low additive levels and, hence, reduced operating costs.

A strong dependency of NO_x removal on the SO_2/NO_x ratio was observed. As shown in Figure 7, the SO_2 level in the flue gas and/or the ratio of SO_2 to NO_x influenced both NO and total NO_x removals, with the higher SO_2 levels clearly improving removals. These findings indicate that combined NO_x/SO_2 removal is best achieved in medium- to high-sulfur coal facilities.

Another key parameter in NO_x removal is the thickness of filter cake maintained on the bags in the baghouse. Both the higher temperatures and the addition of NaOH contributed to the formation of a more porous filter cake, which led to lower pressure drops across the baghouse and longer intervals between bag cleaning. During the extended periods (up to 8 h) between bag cleanings, steadily increasing removals of SO_2, NO, and NO_x were observed (see Figure 8). The highest NO_x removal rates were measured at the end of the filtration periods; however, upon bag cleaning, the NO_x removal rates dropped to a minimum. This gives a cyclic NO_x removal profile that closely parallels the baghouse pressure drop (see Figure 9). Thus, in order to maintain high (40-50%) average NO_x

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[1] Internal equivalence ratio is defined as (Ca + 1/2 Na)/(S + 1/2 NO_x) based on the available alkali content in the feed slurry.

removals, system modifications would be needed to increase the powder handling capacity of the baghouse conveying system to prevent overloading and powder spillage after long filtration cycles.

Chemical analyses of the baghouse powder revealed that the nonsulfite portion of the total sulfur present increased with temperature. The nitrite levels remained relatively constant, while the nitrate concentrations increased significantly with temperature and slightly with the amount of sodium hydroxide addition. Samples taken at the higher temperatures generally had higher total alkalinity. The sodium content in the waste was directly proportional to the amount of sodium hydroxide added; 2-2.4 wt% sodium was found in spent materials from the 5 wt% NaOH addition tests. Detailed leaching tests have not been conducted with these materials and would be needed for future waste disposal considerations.

CONCLUSIONS

Research has been conducted on integrated processes that could lead to relatively low-cost NO_x control retrofits of wet and dry scrubbing technologies. The use of metal chelates in wet scrubber liquors for NO removal is progressing to the pilot-scale phase and has the potential for 50-70% NO_x removal along with 90+% SO_2 removal. The addition of sodium hydroxide to a lime slurry for integrated NO_x removal in spray dryer systems has been demonstrated at a 20-MWe industrial boiler and is ready for commercial-scale testing. NO_x removals of 35-50% are potentially achievable along with 70-90% SO_2 removal depending on the coal being fired. Some modifications to the baghouse conveying system may be needed to accommodate the longer filtration cycles beneficial to NO_x removal. Incorporation of such technologies into wet and dry scrubbing FGD systems provides opportunities for integrated control of SO_2, NO_x, and PM and captures a broad market of existing scrubbers.

DISCLAIMER

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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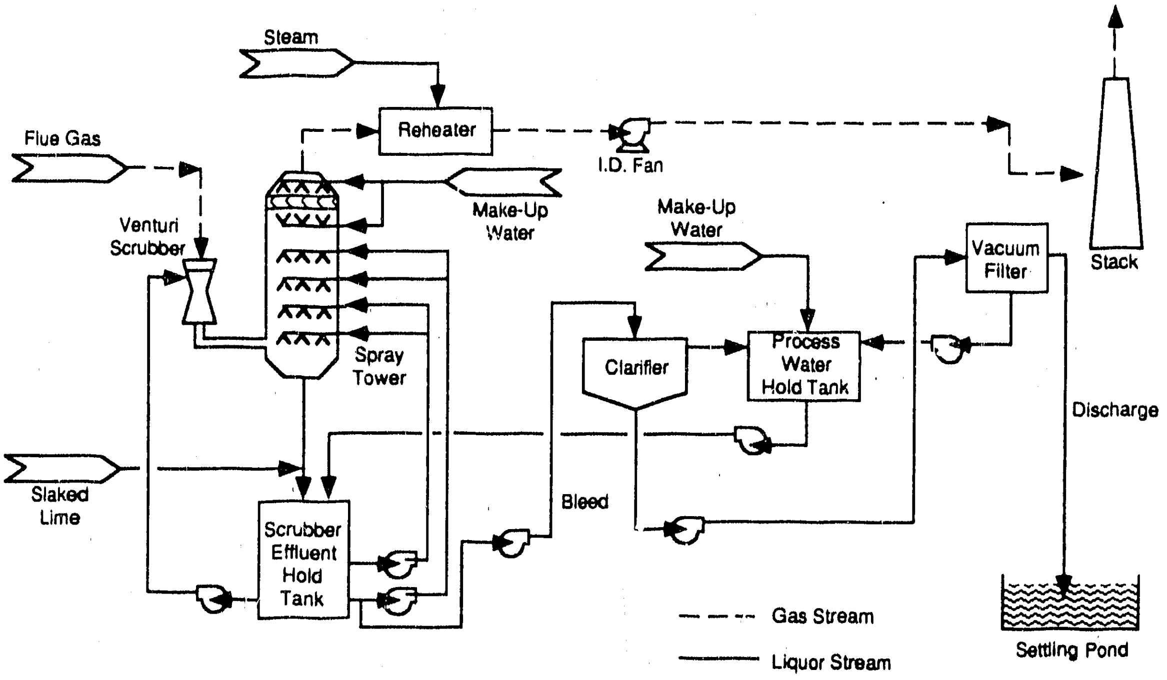

Figure 1. Typical process flow diagram for a wet lime FGD system.

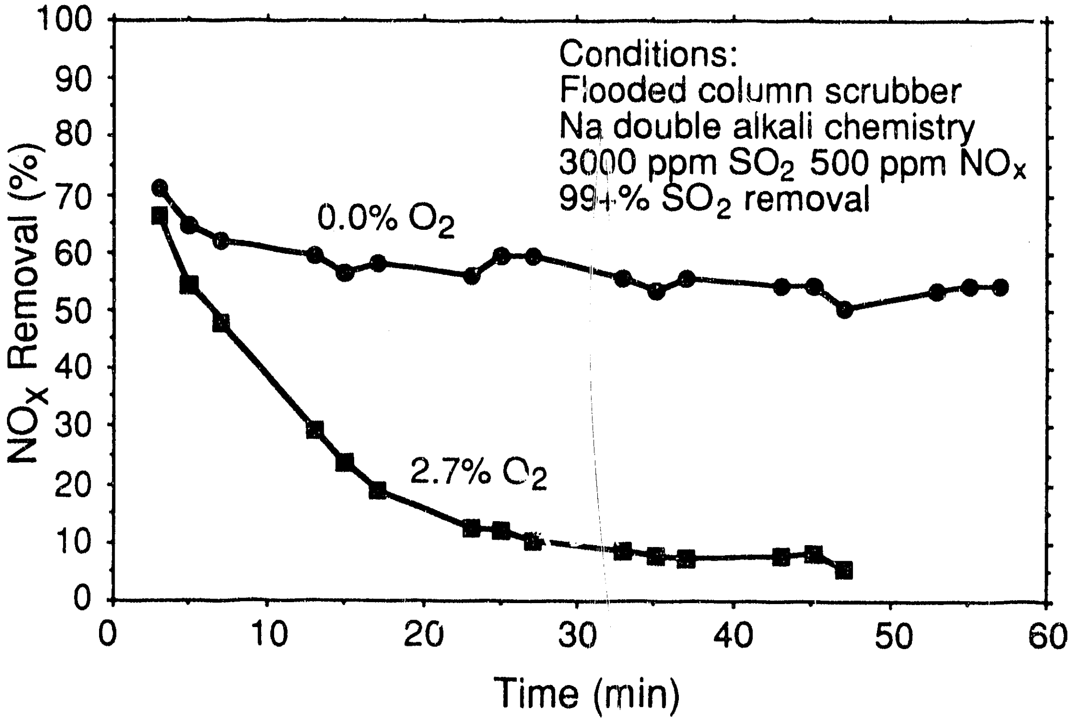

Figure 2. Effect of O_2 concentration on NO_x removal with Fe(II)·EDTA.

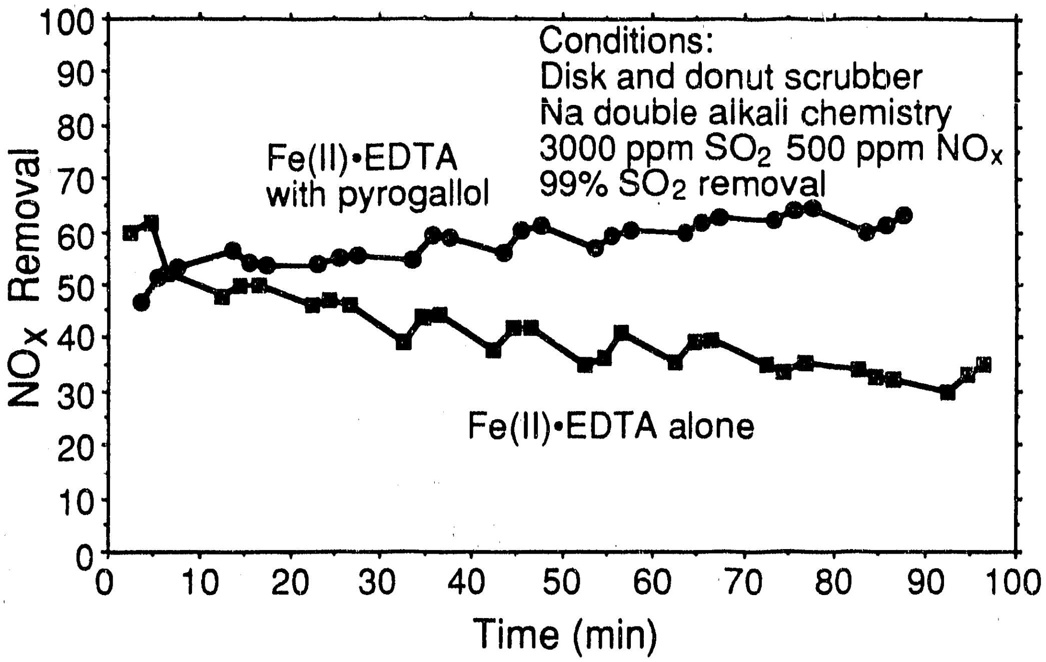

Figure 3. Comparison of NO_x removals with and without the secondary additive pyrogallol.

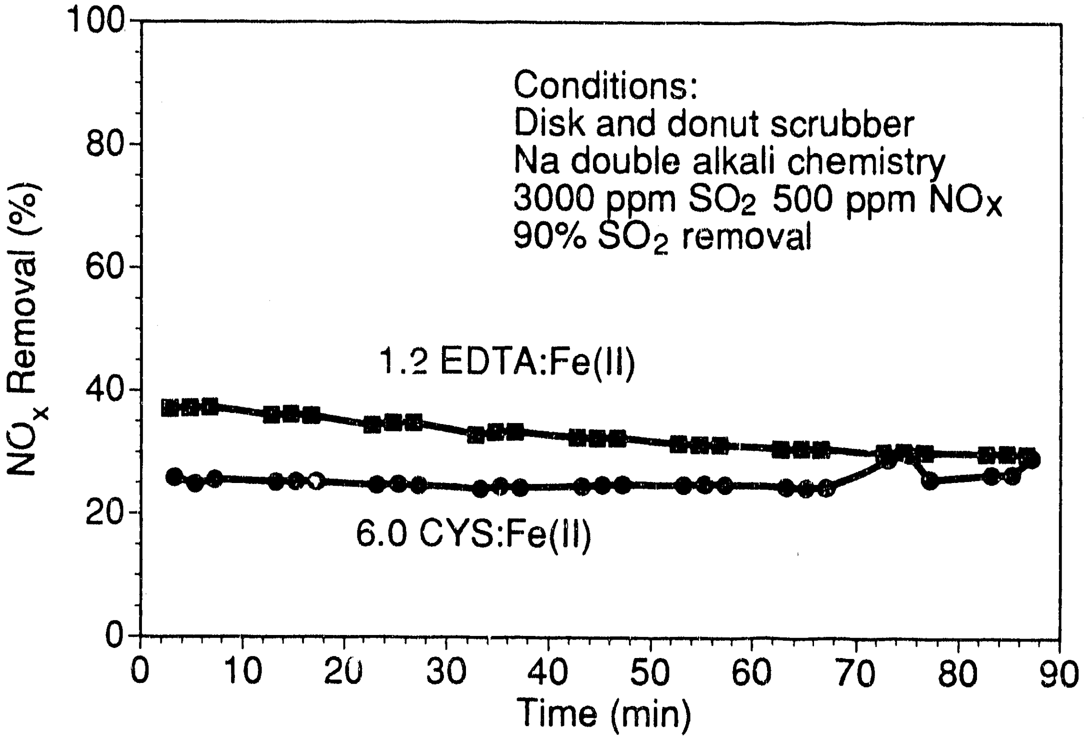

Figure 4. Comparison of NO_x removal performance of Fe(II)·EDTA and Fe(II)·Cysteine.

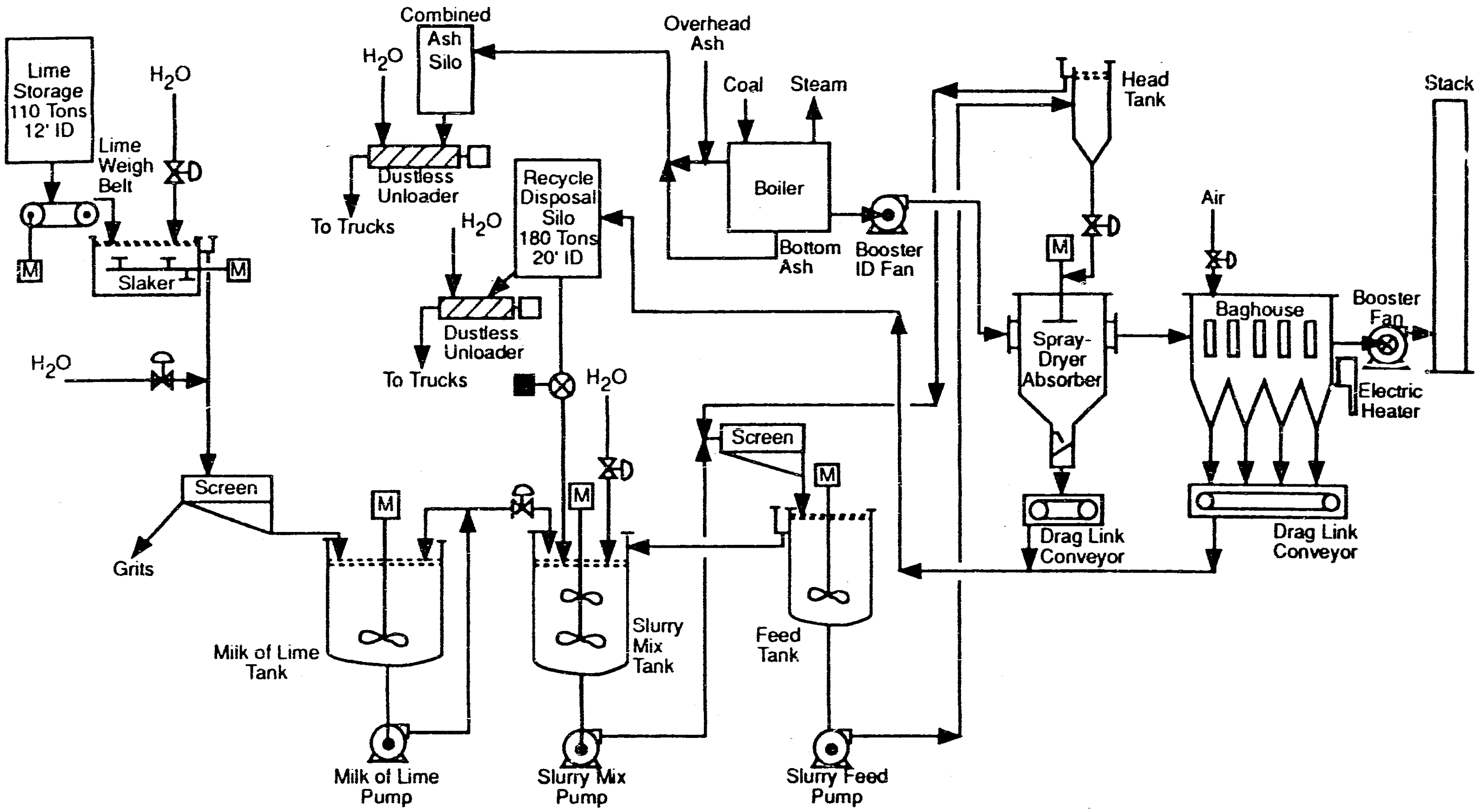

Figure 5. Process flow diagram for ANL spray dryer system.

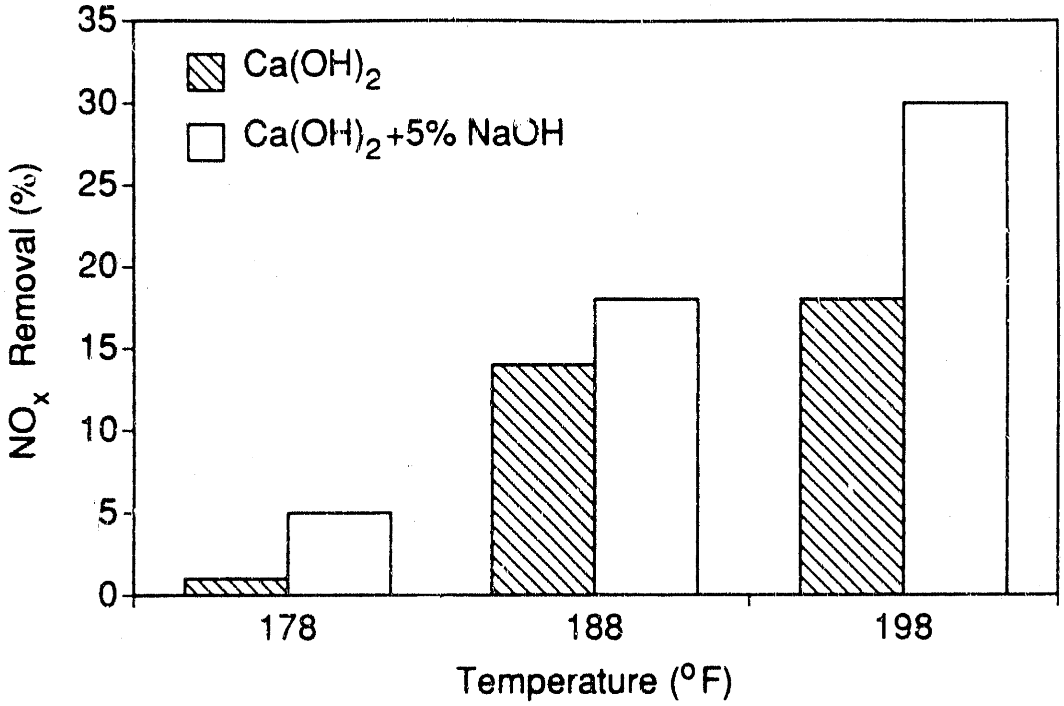

Figure 6. Variation of NO_x removal with spray dryer outlet temperature and sodium hydroxide addition.

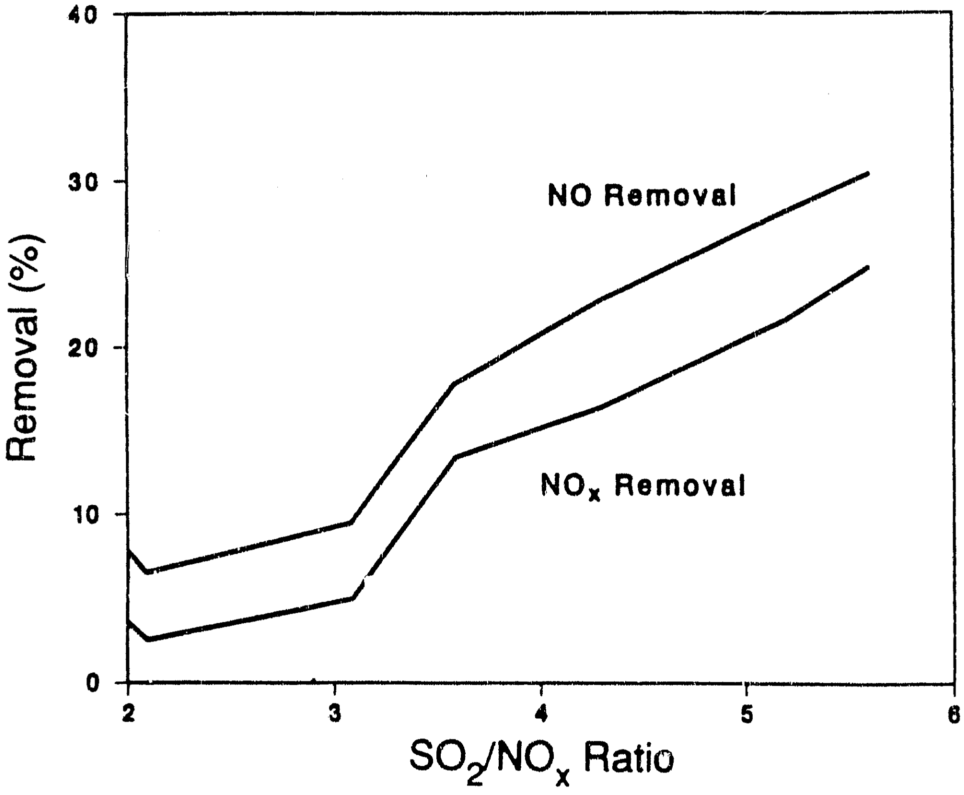

Figure 7. Effect of SO_2/NO_x ratio on NO and NO_x removal.

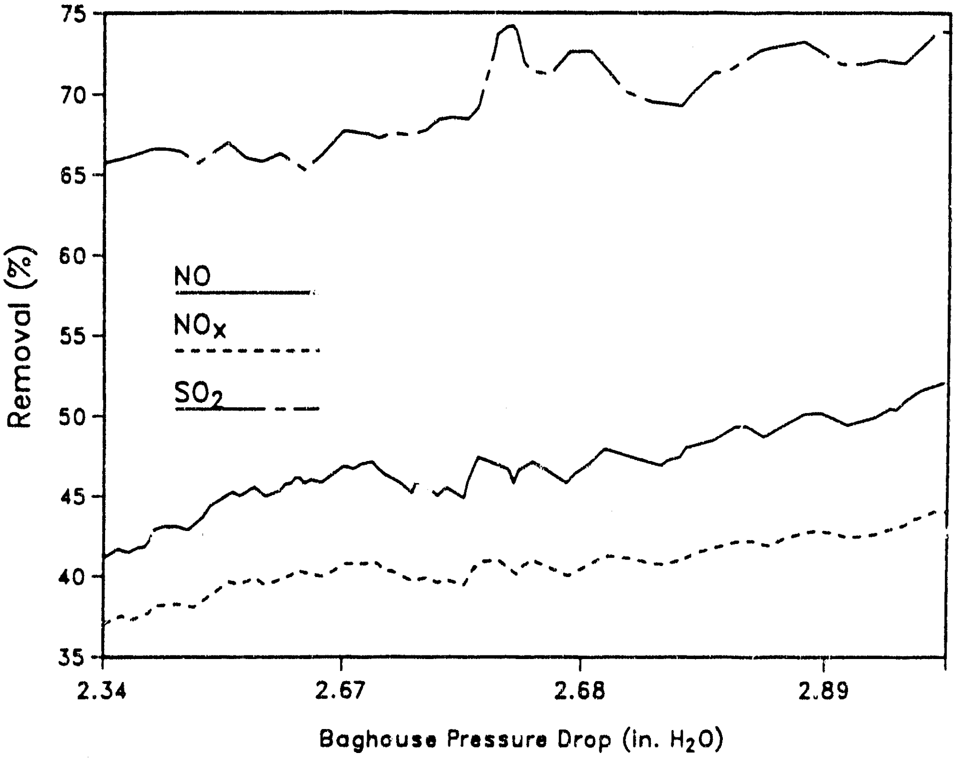

Figure 8. Removal of SO_2, NO, and NO_x with increasing baghouse pressure drop.

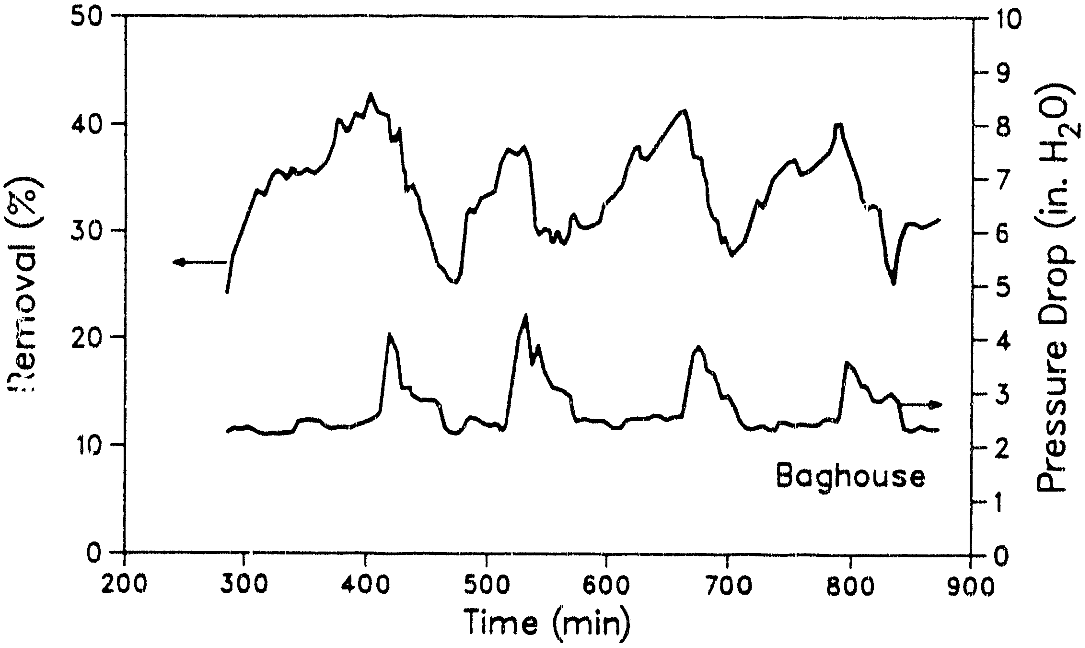

Figure 9. Dependence of NO_x removal on cyclic baghouse pressure drop.

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