Reduction and Removal of SO_2 and NO_x from Simulated Flue Gas using Iron Oxide as Catalyst/Absorbent

Iron oxide supported on alumina is a promising catalyst/absorbent for use in the simultaneous removal of NO_x and SO_x from power plant stack gases. A dry-contacting process is under development which would operate under net reducing conditions at temperatures of 370° to 540°C. Iron oxide is converted to the ferrous state, NO is reduced to N_2 or NH_3, and SO_2 is removed as ferrous sulfide or sulfate. Regeneration with air produces SO_2 and reforms Fe_2O_3.

The reduction of SO_2 by CO and H_2 was studied in fixed-bed reactors to determine the effects of temperature and of the other reactive components of flue gas (excepting fly ash) on the rate of reaction and the products formed. H_2S and COS react with FeO to form FeS. Under readily attainable conditions, virtually complete removal of sulfur compounds was achieved for gas-phase residence times of about 1 to 10 ms. NO and O_2 were also reduced. Conditions under which oxygen poisons the catalyst were determined.

DAVID T. CLAY
and
SCOTT LYNN
Department of Chemical Engineering
University of California
Berkeley, California 94720

SCOPE

Sulfur dioxide and nitric oxide are major air pollutants in the United States. Fossil-fueled power plants are major sources of both. Wet processes for SO_2 removal are currently being developed commercially, but to date no process for simultaneous SO_2 and NO removal has passed the laboratory scale. A dry removal process would be preferred, since this would avoid flue-gas reheating, the problems of contacting the gas with a liquid or slurry, and the crystallization phenomena usually encountered in flue-gas scrubbing. The objective of this study was to develop a dry process which not only achieves high NO and SO_2 removals, but also converts NO to innocuous materials and SO_2 to a salable product and is potentially economical to operate.

The process flow sheet is shown in Figure 1. Iron oxide, supported on alumina, acts as a catalyst for the reduction of both SO_2 and NO by CO and H_2. Simultaneously, it acts as an absorbent for sulfur compounds, converting them to FeS. The catalyst/absorbent is in the form of fine pellets (0.05 to 0.10 mm) and contacts the gas as a falling bed in concurrent flow at 370° to 540°C. The solid is regenerated with air at 675°C to produce a rich stream of SO_2, suitable for conversion to H_2SO_4 or elemental sulfur. Fe_2O_3 is reformed in the particles.

Experiments in fixed-bed reactors using mixtures of helium and one or more reactant gases were run to demonstrate the basic process chemistry, to estimate rates for preliminary design purposes, and to look for interfering reactions. A preliminary estimation of the capital and operating costs of the process was made on the basis of the results obtained.

CONCLUSIONS AND SIGNIFICANCE

The overall reactions listed in Table 1 were shown to proceed rapidly at 370° to 540°C in fixed-bed reactors using pellets of supported iron oxide 3.2 mm × 3.2 mm or particles 0.25 to 0.50 mm diameter. Iron oxide was reduced to the ferrous state, SO_2 was reduced by both CO and H_2, and the sulfur was absorbed as FeS. NO was reduced to a mixture of N_2 and NH_3 by either H_2 or $CO + H_2O$. Stable intermediates in the removal of SO_2, H_2S, and COS were found to react directly with FeO to form FeS. O_2 was also reduced but could lead to poisoning of the catalyst under some conditions of temperature and feed stream composition. Based on breakthrough curves for a bed of particles at 540°C, greater-than-90% removal of SO_2, NO, and O_2 occurred in residence times in the reaction zone of the order of 1 to 10 ms. Intraparticle diffusion was the rate-limiting step in both removal and regeneration reactions.

Oxidation of the sulfided catalyst/absorbent with air at 680°C produced a rich stream of SO_2 and regenerated Fe_2O_3. After three successive cycles, the solid showed no indication of loss of activity. The catalyst/absorbent remained reactive only when the inlet gas stream was net reducing. Formation of $FeSO_4$ from FeS by reaction with O_2 caused poisoning. An excess of CO and/or H_2 minimized $FeSO_4$ formation.

Overall rate data from the fixed-bed reactor were used to estimate the catalyst flow and particle size necessary to treat the flue gas from a 1000-MW power plant in a dispersed-phase, concurrent contactor. The resulting design called for a flow of 0.2 kg catalyst/m^3 flue gas, a one-second residence time, and particles averaging 75 μm. The total flow and the particle characteristics are similar to those in fluid-bed catalytic cracking. The regenerator requires a 5-min. holdup time at about 675°C with this size particle.

Correspondence concerning this paper should be addressed to S. Lynn. D. T. Clay is with Weyerhauser Corporation., Longview, Washington 98622.

An economic evaluation of the process based on a tentative plant design indicates an investment cost of about \$19/kW and an operating cost of about 0.9 mills/kWh for a 1000-MW power plant. The investment includes the cost of a conventional sulfuric acid plant, but no credit was taken for H_2SO_4. These costs are about half those listed for commercially available recovery processes for SO_2 control only (Princiotta and Ponder, 1974) and are appreciably lower than the costs for throwaway processes. Such cost advantages are inherent to a dry recovery process if sufficient catalyst reactivity and lifetime can be demonstrated.

Stack gases from oil- and coal-fired power plants are well known to be major sources of both NO_x and SO_2 (Chilton, 1971; Bartok et al., 1969) which will become of increasing concern in the near future. A significant fraction of the NO derives from nitrogen fixation and can be greatly reduced by combustion modification (Bartok et al., 1969). It has been shown, however, (Pershing et al., 1973; Turner et al., 1972) that the NO deriving from the nitrogen content of the fuel is still well above desirable limits in spite of combustion modification. The SO_2 derives entirely from the fuel; desulfurization is expensive for fuel oil (Princiotta and Ponder, 1974) and a technically unsolved problem for coal. The need to develop processes to control emissions of both is thus clearly established.

The EPA now considers a number of flue-gas scrubbing processes for SO_2 control to be developed to the point of commercial availability (Princiotta and Ponder, 1974). None of these removes a significant amount of the NO. Slack (1973) discusses both wet and dry processes for SO_2 control. He concludes that a dry process would be preferable in concept but that as-yet-unsolved problems of low reactivity have prevented successful applications. No NO-control process, wet or dry, has yet passed the laboratory scale of development.

Most dry processes have proposed the use of a metal oxide to react with SO_2 to form the sulfite (Lowell et al., 1969). In general, a sulfite need be heated only about 300°C to regenerate the oxide. However, in the presence of residual O_2 in the flue gas, some sulfate is invariably formed, which requires heating by 500° to 600°C to regenerate. This large temperature swing has made regenerable metal-oxide processes unattractive. Attention has been focused instead on throwaway processes, with lime, limestone, or dolomite being the only economically feasible materials to consider. Failure has been due primarily to the inability to find the desired combination of high reactivity, high porosity, good handling properties, general availability, and low cost in a naturally occurring material.

Leung and Gidaspow (1974) studied the sorption of NO by supported iron oxide in the presence of O_2 at temperatures of 20° to 350°C. NO_x could be recovered by regeneration with air at 400° to 450°C. Both the rate of sorption and the capacity of the sorbent were low. Ryason and Harkins (1967) reported the simultaneous removal of SO_2 and NO over a copper oxide under reducing conditions in a gas stream. Querido and Short (1973), Okay and Short (1973), and Quinlan et al. (1973) have continued the development of this process. In their conceptual design three fixed-bed reactors, operating at different temperatures, were proposed. The process reportedly produces elemental sulfur and nitrogen from the reduction of SO_2 and NO by CO. Because of the use of fixed beds, the process appears unsuitable for flue gases containing fly ash. The need to recover elemental sulfur by condensation of the vapor requires substantial cooling of the flue gas.

Many metal sulfides are quite stable under reducing conditions at temperatures at which the corresponding sulfates decompose. Haas and Khalafalla (1973) found that FeS and FeS_2 were formed when the reduction of SO_2 to S_2 by CO was catalyzed with iron oxide/alumina. Riesz et al. (1957) showed that NO could oxidize FeS rapidly, giving N_2 and SO_2. Shelef and Kummer (1971) note that many metal oxides catalyse the reduction of NO by CO and H_2. Ammonia formation was found by Shelef and Gandhi (1972) when NO is reduced by H_2 over base metal oxides. These observations are incorporated here in the conceptual design of a dry process for treating power plant stack gases to remove and recover SO_2 and to convert NO_x to innocuous substances.

PROCESS DESCRIPTION

The process being developed combines three fundamental techniques for nitric oxide and sulfur dioxide removal. These are combustion modification, catalytic reduction, and metal-oxide absorption. The process and function of each technique can best be explained by referring to Figure 1.

This figure gives the general layout of a power plant furnace and the proposed process. The furnace is operated under oxidizing conditions to assure that all of the coal or oil is oxidized and no soot is formed. The type of fuel and the burner design dictate the lowest level of excess air allowed to meet this requirement. At a point higher up in the furnace a rich stream of CO and H_2 is introduced to shift the flue gas from net oxidizing to net reducing stoichiometry. This rich CO/H_2 stream could be generated by an adiabatic coal-gasification unit adjacent to the power plant. At least enough CO and H_2 is added so that at equilibrium all of the O_2 would be reduced to CO_2 or H_2O, all of the NO to N_2, and all of the SO_2 to H_2S. Since this fuel addition is made in the furnace, its heating value will be recovered either in the superheater and air preheater sections of the power plant or in the catalyst regenerator.

Between the exit of the superheater and the entrance of the air preheater the flue gas is contacted with the catalyst/absorbent particles. The particles consist of supported iron oxide, which is reduced by CO or H_2 to FeO and both catalyzes the reduction of NO to N_2 or NH_3 and effects the absorption of sulfur as sulfide. The temperatures in this region range from 370° to 540°C. An estimated 1-s flue-gas residence time is required. After the solids and flue gas leave the contactor, they enter mechanical cyclones. These remove the solids from the gas and segregate the catalyst/absorbent material from the fly ash. After the flue gas passes through the economizer and air preheater, electrostatic precipitators remove the fly ash and catalyst fines. The catalyst/absorbent from the cyclones is sent back for reinjection into the flue gas contactor. A portion of this recycle stream is diverted to the regenerator where air is added in a fluid bed to convert the iron sulfide back to the oxide. This generates a rich SO_2 stream that can be used as a feed to an H_2SO_4 or sulfur plant. The regenerated catalyst is fed back to

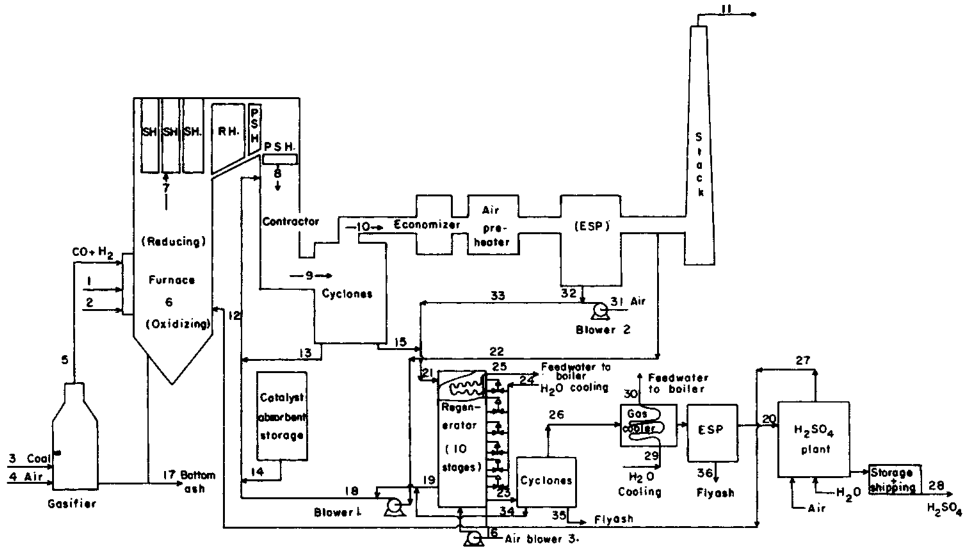

Fig. 1. Conceptual design of NO/SO2 removal process.

the boiler after mixing with the recycle stream.

The primary reactions are listed in Table 1. The catalytic reduction of NO is accomplished by an excess of CO or H_2 in the flue gas. Both N_2 and NH_3 are potential products. All three of the reactions have been shown to proceed over either iron oxide of sulfide. The sulfur compounds are removed by reduction with CO or H_2 to form COS or H_2S. These reduced sulfur compounds react with FeO to form FeS. The first two reactions are the most important since more than 95% of the sulfur will be present initially as SO_2. FeS may react with residual oxygen to form $FeSO_4$.

An excess of reducing agent will be required to achieve high removal levels of both NO and SO_2. The excess reducing agent is oxidized by maintaining an excess of Fe_2O_3 in the recycle solids to avoid emission of CO from the stack. The reactions to remove the excess CO and H_2 are endothermic; the thermal loss associated with their removal is recovered in the regenerator.

In the regenerator, FeS and FeO react exothermically with O_2 to produce a self-sustained reaction. A rich SO_2 stream and the regenerated ferric oxide are produced. The residence time of the solids in the bed is about 300 s. The temperature in the regenerator is maintained at about 675°C by controlling the amount of heat removed from the bed. This temperature is high enough to decompose any iron sulfate which may have been formed. The heat is removed by exchange with boiler feed water and returned to the power plant heat cycle.

TABLE 1. OVERALL CHEMICAL REACTIONS FOR NO/SO2 REMOVAL PROCESS

Absorption/Reduction

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$
$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$
$$2NO + 3H_2O + 5CO \rightarrow 2NH_3 + 5CO_2$$
$$FeO + SO_2 + 3CO \rightarrow FeS + 3CO_2$$
$$FeO + SO_2 + 3H_2 \rightarrow FeS + 3H_2O$$
$$FeO + H_2S \rightarrow FeS + H_2O$$
$$FeO + COS \rightarrow FeS + CO_2$$
$$FeS + 2O_2 \rightarrow FeSO_4$$
$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$
$$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O$$

Regeneration

$$2FeS + 7/2\ O_2 \rightarrow Fe_2O_3 + 2SO_2$$
$$2FeSO_4 \rightarrow Fe_2O_3 + 2SO_2 + 1/2\ O_2$$
$$2FeO + 1/2\ O_2 \rightarrow Fe_2O_3$$

TABLE 2. CATALYST/ABSORBENTS TESTED*

Number	Name	% Metal oxide	Internal surface area (Fresh) S_v (m^2/g)	Internal pore volume V_p (cm^3/g)
Cu-0803T ⅛	Copper Oxide	10% CuO	137	0.42
FE-0301T ⅛	Iron Oxide	20% Fe_2O_3	41	0.31
Ni-0301T ⅛	Nickel Oxide	11% Ni	64	0.32

* Provided by Harshaw Chemical Company.

EXPERIMENTAL SYSTEMS

The catalyst/absorbent materials used in these tests are listed in Table 2. Iron oxide supported on an alumina matrix was the main solid tested. The copper oxide/alumina and nickel oxide/alumina were used for special tests. The particle sizes tested were 3.2 mm × 3.2 mm cylindrical pellets and a screened cut of ground particles in the size range of 0.25 to 0.50 mm.

Fixed-bed, flow-through reactors were used in this study. The largest reactor, 32 mm I.D., is shown in Figure 2. Two other similar reactors, 6.4 mm and 9.5 mm I.D., were used in the latter part of the study to achieve shorter residence times. The first reactor was constructed of type 304 stainless steel (ss) and the latter two were 316 ss. Kearby et al. (1971) and Lamb (1972) reported that these steels were effective catalysts for NO reduction. In this work, however, neither steel was found to be catalytically active, perhaps due to the presence of sulfur compounds.

The overall experimental system has been described in detail elsewhere (Clay, 1974). The individual gases were metered into a mixing manifold through flow meters. Helium was used as the system diluent. This allowed quantitative estimation of N_2 formation when NO was reduced and provided sharper NO peaks on the chromato-

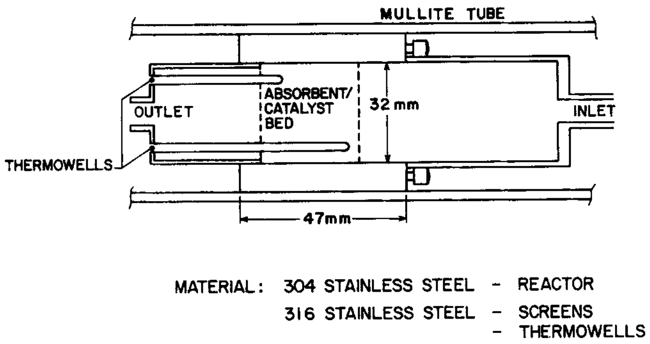

Fig. 2. Experimental reactor–32 mm.

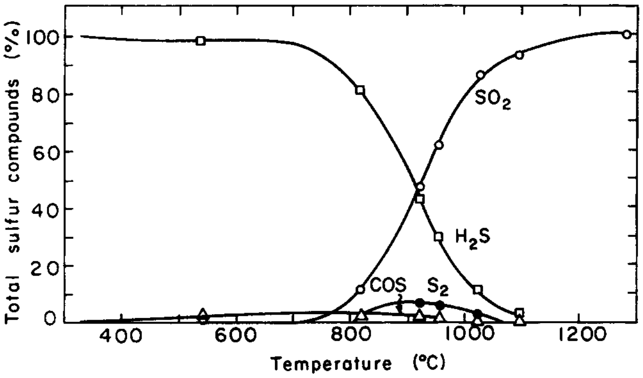

Fig. 3. Equilibrium distribution of sulfur compounds in a typical power plant flue gas.

graph. The He diluent was bubbled through a thermostated water bath to obtain the desired H_2O content.

The 316 ss flow lines in the system were heat-traced to prevent condensation. Continuous inlet and outlet sample purges were maintained during each run. A 6-port Varian Quad-Ring Valve provided periodic sampling of each purge. After the reactor, the main gas stream passed through bubblers to collect NH_3 before it was vented. An enlarged air-cooled section of the outlet line at the exit of the furnace served as a condenser for any sulfur vapor or ammonia-sulfur salts formed in the reaction.

Reactor temperatures were monitored with Chromel/Alumel thermocouples located in 316 ss thermowells. The 32-mm reactor had a 3°C temperature decrease between the reactor outlet and the reactor inlet during reaction. The reactor was located inside a furnace to provide temperature control.

Gas analyses of both inlet and outlet streams were performed by gas chromatography, using two Varian Model 90-P chromatographs in series. Porapak R packing was used in the first column to separate CO_2, N_2O, NH_3, H_2S, COS, SO_2, and H_2O. Molecular sieve 5A was used in the second column to separate H_2, O_2, N_2, NO, and CO. The columns were operated in such a way that the peaks separated in the first did not enter the second. The sensitivity of the analysis for most of these gases was about 100 to 200 ppm. For H_2, NH_3, and H_2O it was about 2000 to 2500 ppm. The progress of most reactions was followed by monitoring both the disappearance of reactive species and the formation of the products of reaction. Mass balances were generally within 10%.

The levels of NO and SO_2 used in the feed stream were generally about 0.5%. This is about twice the level of SO_2 in stack gas from 3% sulfur coal and 5 to 10 times its NO content. The higher level of both gases was necessitated by the sensitivity of the analytical system. To the extent that the removal reactions are diffusion-limited and/or are governed by first-order kinetics, which appeared to be the case for the work reported here, the fractional removals would be independent of concentration level.

RESULTS

The removal reactions for SO_2 and NO were first studied separately. Reactions involving both SO_2 and NO were combined in the next part. Finally, all reactive flue-gas components were present during the last test series. The initial studies were at 370°C with about 0.50 s gas residence time (θ) in the bed. (θ = interstitial bed volume/volumetric flow at bed temperature.) Later studies were at 540°C with residence times of 20 to 40 ms.

SO_2 Removal

The reduction of both SO_2 and NO requires the presence of a reducing gas. Equilibrium calculations were made to determine the stable sulfur species as a function of temperature for a typical flue-gas composition under slightly reducing conditions. It is seen in Figure 3 that H_2S is the primary equilibrium species below 800°C, whereas SO_2 predominates at 1100°C and above. In these calculations the CO_2/H_2O ratio was 1.37 and the initial ratio of

$$\frac{\text{oxidizing equivalents}}{\text{reducing equivalents}} = \frac{3(SO_2)}{(CO) + (H_2)} = 0.521$$

A series of experiments with no catalyst present showed that the homogeneous reduction of SO_2 proceeded to a significant extent only above 1000°C. In these tests the inlet gas contained 0.5% SO_2, 1.6% CO, 1.6% H_2, and 1.7% H_2O and was heated to a given temperature while flowing through the empty reactor. Since the CO_2/H_2O ratio in these tests was 0.088, not 1.37, the equilibrium sulfur species would have been primarily S_2, not H_2S, in the temperature range 900° to 1300°C. No initial CO_2 was used since the progress of the reaction was followed by monitoring its formation. The residence time of the gas at the temperature of each experiment was about 2.4 s, 10 times the high-temperature residence time found in normal boiler furnaces. The experimental and calculated curves are presented in Figure 4. These results show that the reactions of sulfur compounds freeze kinetically at about 1000° to 1100°C in normal flue gases. Therefore, it is expected that at least 95% of the sulfur in the flue gas in this process will be in the form of SO_2 even though

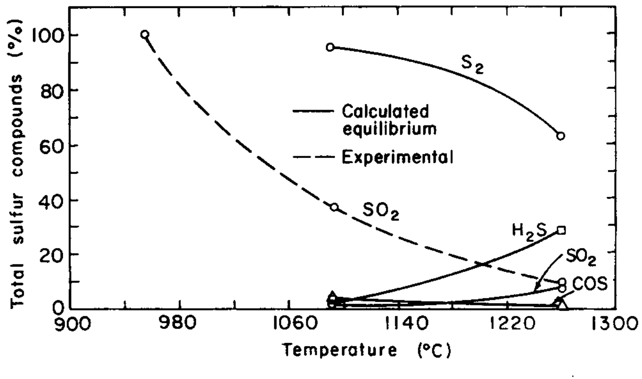

Fig. 4. Comparison of equilibrium and experimental SO_2 under Run No. 28 conditions.

Feed: $[H_2O]$ = 1.95% $[H_2]$ = 1.6%
$[CO]$ = 1.5% $[SO_2]$ = 0.5%

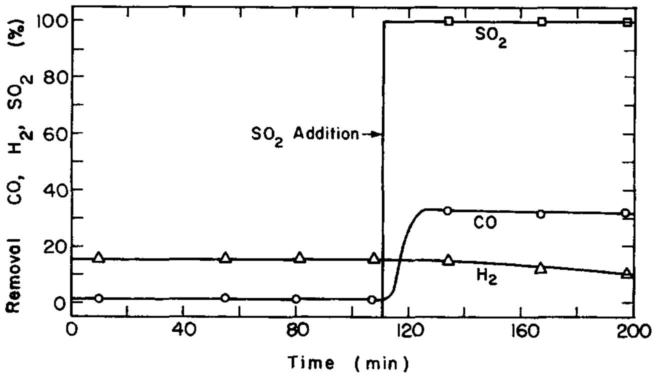

Fig. 5. Reduction of SO_2 by CO and H_2 combined
Run 27d $T = 374°C$ $\theta = 0.43$ s
Feed: $[H_2] = 3.7\%$ 3.2-mm pellets, Fe 301-T
$[CO] = 4.0\%$ $FeO_{1.1}S_{0.15}$ (initial state)
$[SO_2] = 0.45\%$ $FeO_{0.85}S_{0.26}$ (final state)

CO and/or H_2 are present in excess (see Figure 3).

The results of the experiments in which only SO_2, CO, and/or H_2 were fed to the reactor are described in detail elsewhere (Clay, 1974) and will be summarized here. Sulfur sorption as FeS required some prior reduction of Fe_2O_3 to FeO. It was found that a pre-reduction treatment of the catalyst/absorbent pellets greatly increased the rate of reduction of SO_2 at 370°C. When this was not done, reduction of Fe_2O_3 proceeded in addition to reduction of SO_2 at 370° and removal of the latter was hindered. CO was found to be more reactive than H_2 in reducing SO_2 although less reactive in reducing Fe_2O_3, as shown in Figure 5. In this run, catalyst which had previously been partially reduced and slightly sulfided was initially exposed to a CO/H_2 mixture. Continued reduction was effected primarily by H_2. When SO_2 was added to the feed it was nearly completely removed, and its removal was accompanied by a nearly stoichiometrically equivalent increase in CO removal. At the end of the run the oxidation state of the iron had been lowered and its degree of sulfidation had been increased. A high conversion of the iron to FeS resulted in formation of S_2, H_2S, and COS and their detection in the exit gas from the reactor. COS has been postulated by Haas and Khalafalla (1973) to be a reaction intermediate in the reduction of SO_2 to S_2 by CO.

The presence of CO and/or H_2 was found to be essential to maintaining the absorbent activity of the iron oxide. Both FeO and Fe_2O_3 rapidly deactivated when gas containing only SO_2 was passed through the bed at 370°C. Catalyst/absorbent activity returned quite slowly after the flow of CO/H_2 was resumed. This indicates that sulfite formation is probably not part of the sulfur-removal sequence of reactions.

Since H_2S and COS may be present in the flue gas in small amounts, their reactivity with reduced iron oxide was tested. Absorption to form FeS and H_2O or CO_2 was found to be about as rapid as SO_2 reduction.

NO Removal

The reactions of NO, CO, H_2, and H_2O over Fe_2O_3, FeO, and FeS have also been presented in more detail elsewhere (Clay, 1974; Clay and Lynn, 1974) and will be summarized here. NO was found to react rapidly with FeO, less rapidly with FeS, to form N_2 and, in the latter case, SO_2. In the presence of the stoichiometrically required CO, reaction was rapid and the evolution of SO_2 from FeS was eliminated. N_2 was the reduction product; no N_2O was detected. Reduction of NO by H_2 over either FeO_x or FeS was found to result in the formation of varying amounts of NH_3 as well as N_2. The same thing occurred when the reducing agent was CO and H_2O was present. The fraction of NO which is converted to NH_3 is a function of the product of the fraction of iron in the form of FeS and of the ratio of oxidizing agents to reducing agents in the gas. This functionality is illustrated in Figure 6, in which the ammonia selectivity for a number of different runs is correlated. In general, the selectivity for ammonia is favored by high FeS content and low ratios of oxidizing to reducing components in the gas. For the conditions expected for this process the fraction of NO converted to NH_3 should be about 50%. Ammonia selectivity was found to be insensitive to temperature in the range 370° to 590°C even though NH_3 is unstable relative to the elements at the higher temperatures.

Simultaneous Removal

The primary reactive gases in flue gas are NO, SO_2, O_2, H_2, CO, and H_2O. Oxygen would not be expected under ideal conditions in the proposed process since an excess of CO and/or H_2 is to be present, but may nevertheless occur due to poor mixing. Its effect was therefore studied and was found to be of critical importance.

Figure 7 illustrates the results of a typical run containing all of the reactive gases except H_2 in the feed and with net reducing conditions. Small particles were used and the calculated breakthrough time for sulfur compounds, 78 min., was as close to that observed as the analytical system permitted.

From this and other runs, it was estimated that sulfur

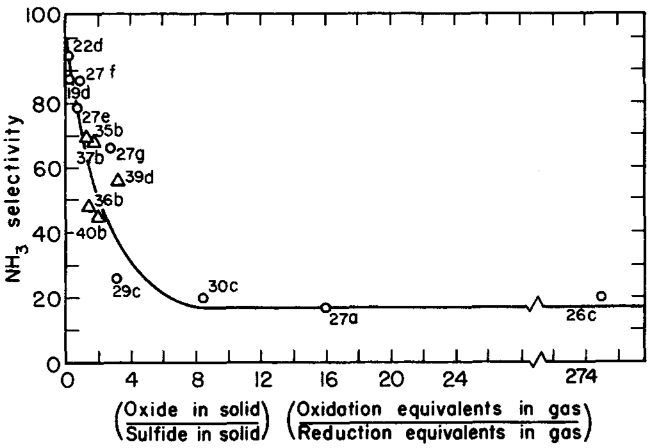

Fig. 6. NH_3 selectivity as a function of solid and gas composition.

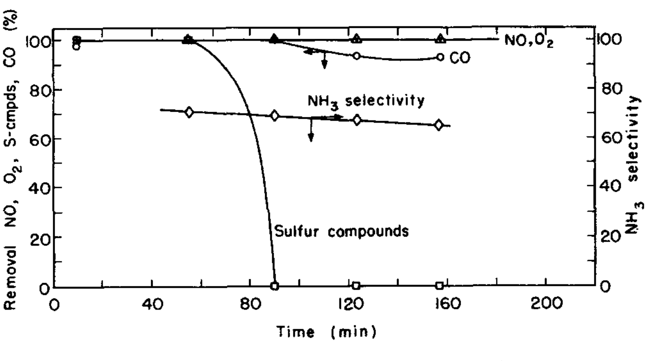

Fig. 7. Simultaneous reduction of NO and SO_2
Run 36b $T = 370°C$ $\theta = 0.034$ s
Feed: $[NO] = 0.50\%$ $[CO] = 3.6\%$
$[SO_2] = 0.50\%$ $[H_2O] = 1.4\%$
$[O_2] = 0.45\%$ 0.5-mm particles, Fe 301-T

breakthrough for this packing occurred only after at least 80% of the iron had been converted to FeS. The actual residence time of the gas in the reaction zone would thus be about 1 to 10 ms. The quantitative estimation of sulfur compounds in the exit gas after breakthrough was made difficult by the presence of the ammonia. $(NH_4)_2SO_3$ and NH_4HS were both identified in the precipitates which formed in the cooler regions of the system after breakthrough. Elemental sulfur was also found occasionally. In the run of Figure 7 complete NO removal was still being observed after 160 min., indicating that FeS is quite effective as a catalyst for NO reduction by CO.

The presence of oxygen at concentrations of about 1% was found to lead to catalyst poisoning or deactivation at 370°C even when the gas composition was net reducing. The appearance of deactivated catalyst was reddish instead of the black of FeO and FeS. Analysis indicated the presence of $FeSO_4$. Slightly poisoned catalyst was completely inactive toward the SO_2 and NO removal reactions, but still catalyzed O_2 reduction. Catalyst operating in a net oxidizing atmosphere lost all activity. In all cases, catalytic activity eventually returned when oxygen was eliminated from the feed gas.

At 540° the catalyst was found to be less sensitive to poisoning by oxygen. While deactivation still occurred under net oxidizing conditions, it did not occur under net reducing conditions even at a high O_2 concentration. Furthermore, the response to changes in feed gas composition was much more rapid at 540°, and one would anticipate that the reaction zone was still smaller (although this could not be determined directly).

Catalyst Regeneration

Under normal process conditions, the sulfur content of the catalyst/absorbent should never become so great that sorption of sulfur compounds ceases. This requires recycling a stream of the solids between the flue-gas contactor and a regenerator. The effectiveness of regeneration with a gas of varying O_2 content was therefore tested for four successive cycles of removal followed by regeneration. The results are presented in Figure 8. It is seen that regeneration appears to have been complete for all conditions tested. Undiluted air thus appears to be satisfactory for this purpose. The time allowed for the regeneration in these tests is not indicative of that which will be required in the process since SO_2 evolution ceased after 5 min. when air was used. The regeneration is a combination of oxidation and thermal decomposition and should proceed at a rate similar to those of the reduction/absorption reactions. No decrepidation of the catalyst particles was observed after this 4-cycle run, but of course far more extensive testing would be required to demonstrate suitable catalyst life for the proposed process.

In the period before sulfur breakthrough during the removal half of the cycles in Figure 8, there was complete removal of O_2, NO, and SO_2 from the feed gas and 80% removal of CO. Sulfur breakthrough was in the form of H_2S and occurred close to the calculated 69 min. Ammonia selectivity during this cyclic test ranged from 53 to 64%.

Ni and Cu Catalysts

Since the NH_3 formed is thermodynamically unstable at 540°C, it would be expected to decompose readily on a suitable catalyst. Nickel has been reported to have such activity (Klimisch and Taylor, 1973). A run was made in the 9.5-mm reactor in which the bed consisted of two sections. The first contained Fe catalyst and the second the Ni catalyst, Table 2, both ground and sized to 0.25 to 0.50 mm. The conditions were the same as in Run 39 (Figure 8). The NH_3 selectivities for two trials were 27% and 41%, somewhat lower than before, but not significantly so. Removal efficiencies were essentially the same.

Quinlan et al. (1973) reported on the simultaneous reduction of SO_2 and NO with CO, H_2, or $CO + H_2O$ to sulfur and nitrogen over a copper oxide/sulfide catalyst. The absence of NH_3 as a product of NO reduction is in sharp contrast to this work. A catalyst identical to theirs, Harshaw Copper Oxide Catalyst, Cu-0803T 1/8, was tested in this study. The catalyst was first reduced to $CuO_{0.15}$ with CO. The inlet gas mixture and resulting gas removals are shown in Figure 9. NO, O_2, and SO_2 were completely removed. In contrast to the iron oxide system, which did not allow escape of any reduced sulfur compounds until nearly saturated, the copper oxide almost

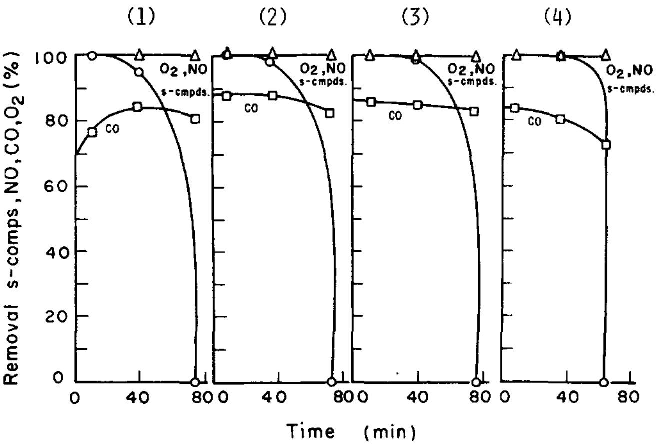

Fig. 8. Cyclic operation of catalyst/absorbent bed. Removal followed by regeneration

Run 39 0.5-mm particles, Fe 301-T $\theta = 0.04$ s
Removal conditions
Feed: $[NO] = 0.50\%$ $[O_2] = 1.0\%$ $[H_2O] = 1.7\%$
$[SO_2] = 0.56\%$ $[CO] = 5.5\%$ $T = 560°C$
Regeneration conditions
1st O_2 @ 4% for 66 min. $T = 670°C$
2nd O_2 @ 2% for 129 min.
3rd O_2 @ 21% for 63 min.

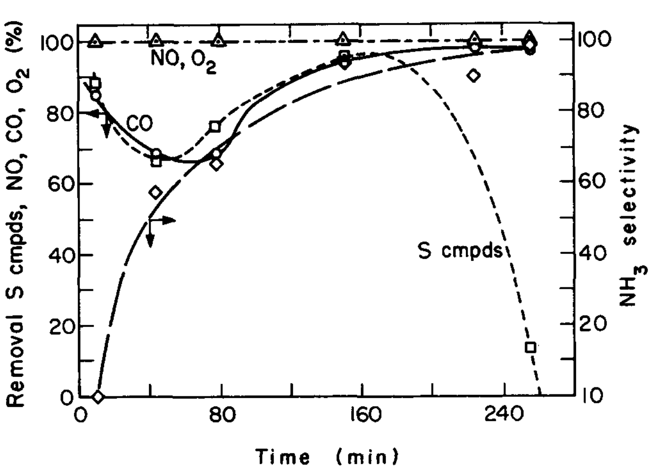

Fig. 9. Simultaneous removal of SO_2, NO, CO, and O_2 over copper oxide catalyst.

Run 33b $T = 538°C$ $\theta = 0.33s$
Feed: $[NO] = 0.50\%$ $[CO] = 4.2\%$
$[SO_2] = 0.50\%$ $[H_2O] = 1.9\%$
$[O_2] = 0.45\%$
3.2-mm pellets, Cu 0803 — T 1/8
$CuO_{.15}$ (initial state) $CuS_{.59}$ (Final state)

immediately released COS. H_2S did not break through until after 150 min. There was only slight N_2 generation during the run. NH_3 was the major product from NO reduction. The average NH_3 selectivity over the run, obtained from the HCl scrubber titration and precipitate analysis, was 73%. A second removal cycle was not conducted on the copper oxide. These tests have demonstrated that although both copper and nickel catalysts are active for the proposed removal reactions neither significantly lowers the NH_3 selectivity nor increases the reaction kinetics relative to iron.

PROCESS DESIGN

These experimental results were used to estimate a feasible catalyst flow and particle size for the design of a process for controlling both NO and SO_2 emissions for a 1000-Mw, coal-fired power plant (Figure 1). The results from the fixed-bed experiments were extrapolated to the plant-scale, dispersed-solids contactor using the following model (Levenspiel, 1962): A gas containing reactive component a is exposed to a catalyst bed of uniform average density ρ_B. Within an element of volume, the rate of change in the bulk gas concentration C_{ag} due to mass transfer to the surface of the catalyst particles is

$$-\frac{d\,C_{ag}}{dT} = k_m S_{ex} \rho_B (C_{ag} - C_{as}) \qquad (1)$$

The flux of a to the catalyst surface is the result of the reaction occurring within the catalyst particles. The use of the effectiveness factor η allows the rate of the reaction within the pore volume to be expressed in terms of the concentration at the particle surface. Equated to the change in bulk gas composition this becomes

$$-\frac{d\,C_{ag}}{dT} = V_p \rho_B k_r \,\eta\, C_{as} \qquad (2)$$

Equations (1) and (2) can be combined to eliminate C_{as} and integrated to yield

$$\frac{C_{ag2}}{C_{ag1}} = \exp\,(-K\rho_B\theta) \qquad (3)$$

where K, the overall rate coefficient, combines the effects of extraparticle convection, intraparticle diffusion, and rate of catalytic reaction:

$$K = (1/k_m\,S_{ex} + 1/V_p k_r \eta)^{-1} \qquad (4)$$

The assumptions implicit in this model after integration are additive mass transfer resistances, constant mass transfer coefficients, noninteraction between diffusing species, and first-order reaction kinetics. If these assumptions are valid, the model is equally applicable to a fixed-bed reactor or to a dispersed-solids contactor.

The precise evaluation of K from experimental data is difficult because the reaction is so fast. However, one may conclude from runs such as that presented in Figure 7 that the reduction of SO_2 was 99% complete after passage of the gas through the reaction zone. This is estimated to have taken 1 to 10 ms in a bed having a density of 1170 kg/m^3. The value of K obtained from these approximations is 0.4 to 4 m^3/kg s. Estimation of the size of the reaction zone for NO reduction is more difficult since both FeO and FeS appear to be effective catalysts. For simplicity, K for NO was assumed to be the same as K for SO_2.

The mass transfer coefficient k_m can be estimated from published correlations for packed beds. The values of Re_p for the run considered above was in the range of 0.3 to 0.6. Sherwood et al. (1975) report that the mass transfer data in this region are quite sparse. The range of Sh to be expected is 0.2 to 2. For SO_2 diffusing through helium at 300° to 500°C to particles 0.25 to 0.50-mm diameter this corresponds to values of $k_m S_{ex}$ of 3 to 30 m^3/kg s. Convective mass transfer resistance would thus appear to play a minor role even in a packed-bed reactor. In the proposed dispersed-solids contactor, Sh will not be less than 2.0, the value for a single sphere in a stagnant, infinite medium.

The effectiveness factor η is related to the Thiele modulus ϕ by the expression (Petersen, 1965)

$$\eta = \frac{3}{\phi}\left[\frac{1}{\tanh\phi} - \frac{1}{\phi}\right] \qquad (5)$$

where

$$\phi = \frac{d_p}{6}\left[\frac{\rho_p S_v k_r}{D_e}\right]^{1/2} \qquad (6)$$

For large values of ϕ (small values of η) the bracketed term in Equation (5) approaches 1 and it is seen that

$$\eta \sim d_p^{-1} \qquad (7)$$

Since $S_{ex} \sim d_p^{-1}$ and $k_m \sim d_p^{-1}$, it is clearly a conservative assumption, for particle sizes smaller than those tested, to make the approximation

$$K \sim d_p^{-1} \qquad (8)$$

Catalyst/absorbent particles averaging 75 μm are large enough and dense enough to allow separation from fly ash in medium-efficiency cyclones (having low pressure drop) yet small enough to have moderate attrition rates due to impact. Equation (3) was used to estimate the effective bed density (ratio of solid to gas flows) necessary for particles this size to achieve 90% SO_2 removal in a contact time of 1 s. A range of 0.1 to 1 kg/m^3 (based on actual stack gas volume @ 540°C) was obtained. A solid/gas flow ratio of 0.2 kg/m^3 was selected for the design basis. This number is clearly not very precise and its refinement will be the subject of further investigation. However, it is reasonable in view of the rate of 0.10 to 0.13 kg/m^3 used in the manganese oxide absorption process (Uno et al., 1971) in which the average particle size is 40 μm and the gas temperature is 120° to 180°C. The flow of catalyst/absorbent to the regenerator is about one-quarter of the total feed to the flue-gas contactor, so that about three-quarters of the solids leaving the contactor is recycled.

Material and heat balances were made on the system assuming 90% removal of the SO_2 and NO due to operation of both the furnace and the gasifier. Estimates were made of the costs of construction and operation (Clay, 1974). The economic analysis of the system showed the process to be competitive with existing processes which control only SO_2. Operating costs for the 1000-MW unit were estimated to be 0.9 mills/kWh. The capital investment was estimated at \$19/kW. This includes the cost for the H_2SO_4 plant but does not include credit for its sale. Princiotta and Ponder (1974) report operating costs for commercially offered SO_2-removal processes ranging from 1.2 to 2.8 mills/kWh and capital costs from \$26/kW to \$68/kW. Although the design of the proposed process is quite tentative, it was made conservatively and appears to be competitive with existing systems (which remove SO_x only).

There are a number of advantages inherent to a process of this type which lead to the improved economics. First, in spite of the use of the coal gasifier, the overall thermal efficiency of the system (including the heat recovery in the regenerator) is actually improved because excess air in the stack is eliminated. Of course, no reheat for the stack gas is required. Second, the contactor is no larger than the flue-gas scrubbers which have been developed and is much simpler in geometry. The handling and transport of the catalyst/absorbent is established technology, being quite similar in scale to that in fluid bed catalytic cracking. Finally, the costly holding tanks, scaling problems, and waste disposal requirements common to the wet scrubbing processes are eliminated.

A potential disadvantage is the emission of ammonia at 300 to 400 ppm in the stack gas. However, NH_3 is not reactive in the photochemical smog cycle (Robinson and Robbins, 1972). Instead it neutralizes acidic aerosols, reducing their adverse effects. Furthermore, the molar rate of generation of NH_3 by natural decay processes is about 60 times greater than the sum of all current man-made NO emissions (Robinson and Robbins, 1972). Finally, the BAAPCD (1972) has set a limit of 2500 ppm NH_3 for large industrial stacks, which is well above any potential emission from this process. Clearly, however, the ammonia question is one which would eventually require resolution.

ACKNOWLEDGMENT

Fellowship support for DTC was provided by the National Science Foundation, the Environmental Protection Agency, and the Atomic Energy Commission during the course of this project.

NOTATION

a = reactive species
C_{ag} = bulk gas concentration of a, mol/m^3
C_{ag1} = value of C_{ag} at reactor inlet
C_{ag2} = value of C_{ag} at reactor outlet
C_{as} = value of C_a at particle surface
d_p = particle diameter, m
D_a = diffusivity of a in bulk gas, m^2/s
D_{ea} = effective diffusivity of a within particle, m^2/s
k_m = extra-particle mass-transfer coefficient, m/s
k_r = first-order reaction rate constant at catalyst surfact, s^{-1}
K = overall rate coefficient (Equation (4)), m^3/kg s
Re_p = particle Reynolds number, $d_p v \rho_g/\mu_g$
S_{ex} = specific external area of particles, $= 6/d_p\rho_p$, m^2/kg
S_v = specific surface area of pores, m^2/kg
Sh = Sherwood number, $k_m d_p/D_a$
t = time, s
v = velocity of gas relative to particles, m/s
V_p = specific pore volume inside particles, m^2/kg

Greek Letters

μ = effectiveness factor
θ = residence time of gas in reaction zone, s
μ_g = viscosity of gas, kg/m s
ρ_B = bed density or ratio of solid to gas flows, kg/m^3
ρ_g = gas density, kg/m^3
ρ_p = particle density, kg/m^3
ϕ = Thiele modulus, Equation (6)

LITERATURE CITED

BAAPCD, Amendment to Regulation 2, Div. 15-Odorous Substances, Bay Area Air Pollut. Control District (1972).

Bartok, W., A. R. Crawford, A. R. Cunningham, H. J. Hall, E. H. Manny, and A. Skopp, "Systems Study of Nitrogen Oxide Control Methods for Stationary Sources-Volume II," Nat. Air Pollution Control Assoc. (1969).

Chilton, T. H., "Reducing SO_2 Emission from Stationary Sources", in Tech. Manual *Sulfur & SO_2 Development, Am. Inst. Chem. Engrs.*, New York (1971).

Clay, D. T., Ph.D. thesis, "Development of a Feasible Process for the Simultaneous Removal of Nitrogen Oxides and Sulfur Oxides from Fossil Fuel Burning Power Plants," Univ. California, Berkeley (1974); also Lawrence Berkeley Lab. Report 3059 by D. T. Clay, and S. Lynn (1974).

Clay, D. T., and S. Lynn,"Iron Catalysed Reduction of NO by CO and H_2 in Simulated Flue Gas," paper presented at General Motors Symp. "The Catalytic Chemistry of Nitrogen Oxides," (1974) in press.

Haas, L. A., and S. E. Khalafalla, "Kinetic Evidence of a Reactive Intermediate in Reduction of SO_2 with CO," *J. Catalysis*, **29**, 264 (1973).

Kearby, K., N. Miller, A. K. S. Raman, and J. Vardi, "Catalytic Conversion of Exhaust Gas Impurities," U.S. Patent 3,565,574 (Feb. 23, 1971).

Klimisch, R. L., and K. C. Taylor, "Ammonia Intermediacy as a Basis for Catalyst Selection for Nitric Oxide Reduction," *Environ. Sci. Tech.*, **7**, 127 (1973).

Lamb, A., and E. L. Tollefson, "Catalytic Reduction of Nitric Oxide in Low Concentration High Velocity Gas Streams," paper presented at 22nd. Can. Chem. Eng. Conf. "Catalysis and Sorption in Air Pollution Control (1972).

Levenspiel, O., *Chemical Reaction Engineering*, Wiley, New York (1962).

Lowell, P. S., K. Schwitzgabel, T. B. Parsons, and K. J. Sladek, "Selection of Metal Oxides for Removing SO_2 from Flue Gas," *Ing. Eng. Chem. Process Design Develop.*, **10**, 384 (1971).

Okay, V. D., and W. L. Short, "Effect of Water on Sulfur Dioxide Reduction by Carbon Monoxide," *Ind. Eng. Chem. Design Develop.*, **12**, 291 (1973).

Pershing, D. W., G. B. Martin, and E. E. Berkau, "Influence of Design Variables on the Production of Thermal and Fuel NO From Residual Oil and Coal Combustion," *AIChE Symp. Ser. No. 148*, **71**, 18 (1975).

Petersen, E. E., *Chemical Reaction Analysis*, Prentice-Hall, Englewood Cliffs, N. J. (1965).

Princiotta, F. T., and W. H. Ponder, "Current Status of SO_2 Control Technology," paper presented at the Lawrence Berkeley Lab. Seminar entitled *Sulfur, Energy and Environment* (1974).

Querido, R., and W. L. Short, "Removal of Sulfur Dioxide from Stack Gases by Catalytic Reduction to Elemental Sulfur with Carbon Monoxide," *Ind. Eng. Chem. Process Design Develop.*, **12**, 10 (1973).

Quinlan, C. W., V. C. Okay, and J. R. Kittrell, "Simultaneous Catalytic Reduction of Nitric Oxide and Sulfur Dioxide by Carbon Monoxide, *ibid.*, 359.

Riesz, C. H., F. L. Morritz, and K. D. Franson, "Catalytic Decomposition of Nitric Oxide," Air Pollution Foundation of Los Angeles Report No. 20 (1957).

Robinson, E., and R. C. Robbins, "Emissions, Concentrations, and Fate of Gaseous Atmospheric Pollutants," in *Air Pollution Control*, W. Strauss, (Ed)., Interscience, New York (1972).

Ryason, P. R., and J. Harkins, "Studies on a New Method of Simultaneously Removing Sulfur Dioxide and Oxides of Nitrogen from Combustion Gases," *J. Air. Poll. Cont. Assoc.*, **17**, 796 (1967).

Shelef, M., and J. T. Kummer, "The Behavior of Nitric Oxide in Heterogeneous Catalytic Reactions,"*AIChE Symp. Ser. No. 115*, **67**, 74 (1971).

Shelef, M., and H. S. Gandhi, "Ammonia Formation in Catalytic Reduction of Nitric Oxide by Molecular Hydrogen. I. Base Metal Oxide Catalysts," *Ind. Eng. Chem. Product Research Develop.*, **11**, 2 (1972).

Sherwood, T. K., R. L. Pigford, and C. R. Wilke, *Mass Transfer*, McGraw-Hill, New York, 1975.

Slack, A. V., "Removing SO_2 from Stack Gases," *Environ. Sci. Tech.*, **7**, 110 (1973).

Turner, D. W., R. L. Andrews, and C. W. Siegmund, "Influence of Combustion Modification and Fuel Nitrogen Content on Nitrogen Oxides Emissions from Fuel Oil Combustion," *AIChE Symp. Ser. No. 126*, **68**, 55 (1972).

Manuscript received November 5, 1974; revision received and accepted January 24, 1975.