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Integrated Tests for Removal of Nitric Oxide with Iron Thiochelate in Wet Flue Gas Desulfurization Systems

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Wet flue gas desulfurization scrubbers can be retrofitted for combined removal of SO$_2$ and NO$_x$ from flue gas by adding a newly developed iron(II) thiochelate to limestone slurries. This additive enhances the solubility of NO in limestone slurries by binding NO to form iron nitrosyl thiochelates. The bound NO is then converted to an ammonium ion by iron metal, regenerating the active iron(II) catalyst for continued NO capture. The conditions of the chemical regeneration of iron(II) thiochelate have been studied. This chemical reduction method is efficient, simple, and cost-effective. Integrated tests of this new iron additive on a bench-scale system have been conducted. A turbulent contact absorber was employed to test simultaneous removal of NO and SO$_2$ with iron(II) thiochelate in a limestone slurry. The steady-state NO removal efficiency depends on the operating conditions of an absorber, the iron chelate concentration, the fraction of the flow diverted for regeneration, and the conditions used in the regeneration reactor. The bench-scale test results were used to develop a prediction of the performance of a full-scale spray absorber.

Introduction

Wet flue gas desulfurization (FGD) scrubbers can efficiently control SO$_2$ emissions but are incapable of removing water-insoluble nitric oxide. Modification of the existing limestone scrubbers to allow simultaneous removal of NO$_x$ is very desirable, which would eliminate additional capital costs required in a separate NO$_x$ control scheme.

One approach (*1–4*) that has been developed involves the addition of iron(II)(EDTA), (EDTA, ethylenediaminetetraacetate) in scrubbing liquor to promote the solubility of NO by the formation of iron(II)(EDTA)NO. The bound NO reacts with sulfite/bisulfite ions (from the dissolution of SO$_2$) and is then converted to N$_2$O and nitrogen–sulfur

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compounds. Subsequently, iron(II)(EDTA) is regenerated. However, there are many drawbacks associated with this approach. One problem is the difficulty in the removal of nitrogen–sulfur compounds from the liquor due to their high solubilities in water. Another problem is the ease of oxidation of iron(II)(EDTA) by oxygen to form iron(III)-(EDTA), which is not capable of binding NO. While iron-(III)(EDTA) can be reduced to iron(II)(EDTA) by sulfite/bisulfite ions, the regeneration rate is slow because of small rate constants and low concentrations of sulfite/bisulfite ions in limestone slurries. As a result, the concentration of the active iron(II)(EDTA) in solutions is low, and thus an adequate NO removal efficiency cannot be sustained.

We have recently developed a new iron(II) thiochelate compound for use in limestone scrubbers to control NO emissions (*5, 6*). This iron(II) compound is iron(II)(DMPS)$_2$, where DMPS is 2,3-dimercapto-1-propanesulfonate (HS-CH$_2$CH(SH)CH$_2$SO$_3^-$). The use of this new additive creates different and simpler scrubber chemistry compared to that using iron(II)(EDTA). The iron(II)(DMPS)$_2$ is more resistant to oxidation by oxygen than iron(II)(EDTA). In addition, the DMPS can maintain the iron in the active iron(II) oxidation state, resulting in higher NO absorption efficiency. Furthermore, the iron(II)(DMPS)$_2$ can bind NO with a large equilibrium constant, producing a very stable nitrosyl complex that does not react with sulfite/bisulfite ions. As a result, undesirable nitrogen–sulfur byproducts are not produced in the iron(II)(DMPS)$_2$ system. In addition, iron-(II)(DMPS)$_2$ is very soluble in water, has a low vapor pressure, and does not undergo thermal decomposition at temperatures below 160 °C.

This paper reports the results of tests on an integrated bench-scale turbulent contact absorber (TCA) scrubber system. A new method of regeneration of iron chelates for re-use has been developed. Parametric studies of the absorption efficiency of NO have been conducted, and the conditions of the chemical regeneration of iron(II) thiochelate have been investigated. Based on the bench-scale test results, a prediction of the performance of a full-scale spray absorber has been made.

Experimental Section

A 10 cm diameter, 130 cm long bench-scale spray absorber was used for the measurements reported here. The small column diameter causes the spray droplets to be intercepted by the wall shortly after formation, and it is difficult to measure the gas–liquid interfacial area. We used a turbulent contact absorber (TCA) arrangement so the data from the absorber could be used to predict the NO removal efficiency in a full-scale spray absorber. In a TCA system, beds of low density spheres are wetted by the spray of scrubbing liquor and fluidized by the upward gas flow. The spheres used here are 1 cm diameter hollow plastic balls. The TCA system avoids problems with plugging that can occur in packed absorber systems and is suitable for limestone FGD systems. There are four 13 cm high stages in the TCA used in this study.

To prepare the gas mixture for the system, liquid nitrogen from a 160-L Dewar flask flowed through a vaporizer and mixed with compressed air to obtain a flow of about 15 cfm
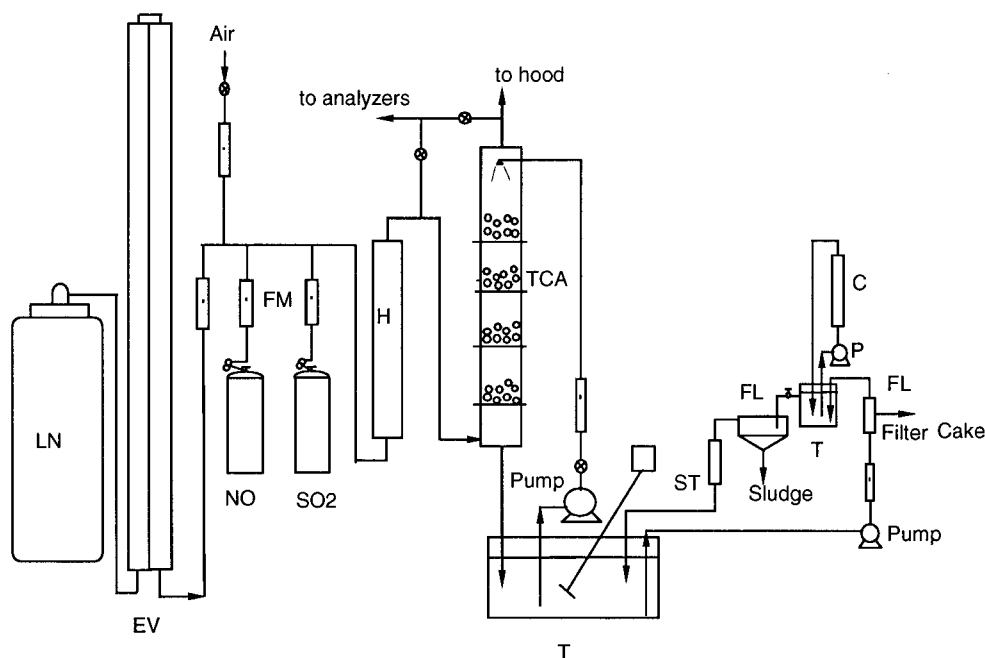
FIGURE 1. Schematic diagram of the integrated bench-scale scrubber system used in this study: LN, liquid nitrogen; EV, evaporator; FM, flowmeters; H, heater; TCA, turbulent contact absorber; T, holding tanks; ST, ammonia stripper; FL, filters; C, column with iron chips.

with the desired oxygen concentration. Small flows of NO and SO_2 were blended in to give concentrations of 100–600 ppm and 1500–2500 ppm, respectively. The gas flowed through an electric air heater to raise the temperature to about 150 °C and then into the base of the TCA absorber. A 40-L holding tank acted as a reservoir for the scrubbing liquor circulating through the absorber and was regulated at 50–55 °C. Two liquid flowmeters (for absorption and regeneration, respectively) monitored the flows of the scrubbing liquor, which consisted of iron chelate-containing limestone slurry. The liquor was pumped to the top of the absorber through a spray nozzle, and gravity feed returned it to the reservoir. The pH of the scrubbing liquor was controlled by feeding a concentrated aqueous limestone/lime slurry to the holding tank. The pH range studied was between 4.5 and 7, which was found to be a suitable range in a previous study (6). Figure 1 illustrates a schematic diagram of the bench-scale scrubber system.

A slip stream of liquor was pumped out from the holding tank to the regeneration system. This system consisted of a cylindrical reactor where the chemical reducing agent was added to reduce the complexed NO to ammonium ion and to reduce the oxidized DMPS back to the reduced DMPS. Elemental iron was used as the reducing agent. The solids ($CaSO_3$, $CaSO_4$, and $CaCO_3$) in the slip stream liquor were removed by filtration prior to regeneration. The filtrate was collected in a 3.5-L regeneration holding tank. The pH in the regeneration holding tank was controlled at a range of 4–5 by small additions of NaOH with a pH control system (Cole-Parmer Series 7142). This offset the loss of hydroxide due to precipitation of iron hydroxides. The liquor was pumped through a 60 mm diameter by 250 mm column loaded with 2400 g of iron chips and recirculated between the regeneration holding tank and the column. The temperature of the regeneration holding tank was maintained at 50–55 °C. After regeneration, the iron(II)(DMPS)$_2$ solution containing additional ferrous ion flowed to the clarifier, which was used to remove the excess iron by precipitation of iron hydroxides at a pH

range of 6–7. The final step of the regeneration was air stripping to remove ammonium ions from the scrubbing liquor. The regenerated iron(II)(DMPS)$_2$ solution was then returned to the scrubbing liquor holding tank for re-use. The makeup limestone was provided by the slurry added for pH adjustment.
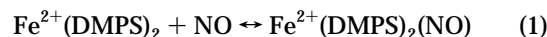
The inlets for the NO_x chemiluminescent analyzer and the SO_2 fluorescent analyzer could be connected to the gas stream at various points along the system. The NO and SO_2 concentrations could thus be measured, and the effectiveness of the absorber operation could be evaluated. Scrubbing liquors were analyzed by ion chromatography and high-performance liquid chromatography (HPLC) and UV–visible, infrared, and Raman spectroscopy.

The concentrations of ferrous ion and total iron in solution were determined by the 1,10-phenanthroline colorimetry method using 510 and 396 nm (7). Solution samples were diluted and acidified for measurement, and it was not possible to discriminate between free ferrous ion and ferrous ion bound to DMPS.
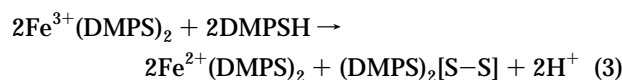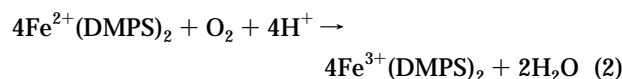
Results and Discussion

The integrated process of NO removal by iron(II)(DMPS)$_2$ and regeneration by elemental iron involves several reactions. These reactions may be summarized as follows:
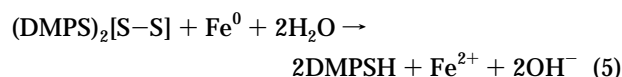
absorption:

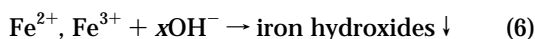$$Fe^{2+}(DMPS)_2 + NO \leftrightarrow Fe^{2+}(DMPS)_2(NO) \qquad (1)$$

oxidation:

$$4Fe^{2+}(DMPS)_2 + O_2 + 4H^+ \rightarrow$$
$$4Fe^{3+}(DMPS)_2 + 2H_2O \quad (2)$$

$$2Fe^{3+}(DMPS)_2 + 2DMPSH \rightarrow$$
$$2Fe^{2+}(DMPS)_2 + (DMPS)_2[S-S] + 2H^+ \quad (3)$$

regeneration:

$$Fe^{2+}(DMPS)_2(NO) + 2.5\,Fe^0 + 6H^+ \rightarrow$$
$$Fe^{2+}(DMPS)_2 + 2.5Fe^{2+} + NH_4^+ + H_2O \quad (4)$$

$$(DMPS)_2[S-S] + Fe^0 + 2H_2O \rightarrow$$
$$2DMPSH + Fe^{2+} + 2OH^- \quad (5)$$

removal of excess iron:

$$Fe^{2+},\ Fe^{3+} + xOH^- \rightarrow \text{iron hydroxides} \downarrow \quad (6)$$
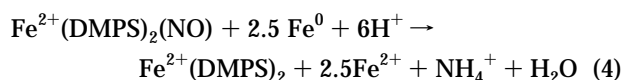
Absorption. The low solubility of NO in water causes the rate of NO removal to be a liquid film-controlled process (*4, 6, 8*). A mathematical model of the process by which NO is absorbed by metal chelate has been derived. The removal efficiency of NO in terms of number of transfer units (NTU) can be expressed as follows:

$$NTU = -\ln\left[1 - \frac{\%\ \text{removal}}{100}\right] =$$
$$\{(k_1[\text{iron(II)(L)}]D_{NO})^{1/2}/(H/P_T)\}\{aZ/P_M V\} \quad (7)$$

The variables in the equation are as follows: k_1 is the rate constant for reaction 1; [iron(II)(L)] is the concentration of iron(II) chelate; D_{NO} is the diffusivity of dissolved NO; H is Henry's constant of NO; P_T is the total pressure of flue gas (1 atm); a is the gas−liquid interfacial area per volume of contact zone; Z is the length of gas−liquid contact zone; P_M is the molar density of flue gas; and V is the flue gas velocity in the absorber. This equation indicates that the NTU should be proportional to the square root of [iron-(II)(L)], linearly proportional to a and Z, and inversely proportional to V. The value a can be better determined with a TCA than with a spray absorber, especially with small diameter systems (*9*). The TCA is known to have a high gas−liquid contact area and a high superficial gas velocity. We can calculate the NTU for a full-scale absorber using this equation if we first obtain a value of the NTU from a bench-scale test. With a value for the NTU, we can then predict the efficiency of NO removal in a full-scale scrubber.

A summary of the experimental results obtained with the TCA system are as follows:

(1) The removal efficiency of NO increases with an increase in L/G. With 47 mM iron(II)(DMPS)$_2$, the TCA achieves removal efficiencies of 63% and 53% at L/G values of 118 and 70 gpm/1000 acfm (15.8 and 9.4 L/m³), respectively, as shown in Figure 2.

(2) The removal efficiency of NO is independent of the concentration of NO over the range of 100−400 ppm.

(3) The removal efficiency of NO increases with an increase in the iron(II)(DMPS)$_2$ concentration over the range of 10−50 mM.

From the results of TCA experiments, we have developed predictions of the performance of a full-scale wet limestone spray absorber, as shown in Table 1. The bench-scale TCA results indicate that a NO removal efficiency of 70% is achieved at an "a" value of 118 ft²/ft³ (36 m²/m³), L/G of 140 gpm/1000 acfm (18.7 L/m³), and Z of 1.83 ft (0.55 m). Based on the mathematical model, one can calculate a to be around 15 ft²/ft³ (4.6 m²/m³) if the droplet diameter is 2 mm. Assuming a Z of 60 ft (18 m) and L/G of 140 gpm/1000 acfm (18.7 L/m³), the NTU is calculated to be 0.5,
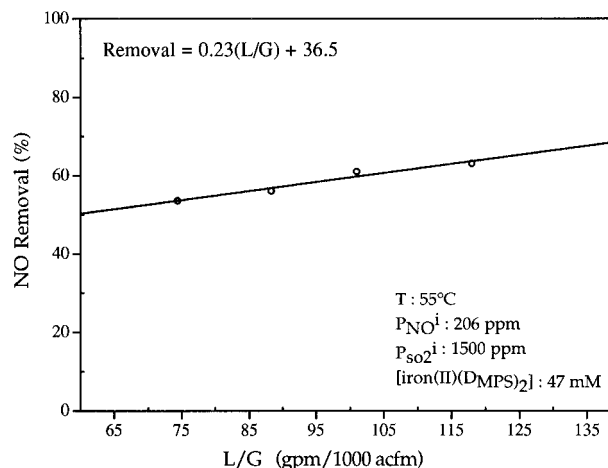

FIGURE 2. Effect of the liquid/gas ratio (L/G) on NO removal efficiency.

TABLE 1

Extrapolation of Bench-Scale Results to Full Scale System

absorber	d_p (mm)	a (ft²/ft³)	Z (ft)	V (ft/s)	NTU	NO (% removal)[a]
10 cm diameter TCA		118	1.83	1	1.2	70
countercurrent spray absorber	2	15	40	10	0.33	28
	2	15	60	10	0.50	40
	1.5	35	40	10	0.78	54
	1.5	35	60	10	1.17	69

[a] For [Fe(II)(DMPS)$_2$] = 47 mM and L/G = 140 gpm/1000 acfm = 18.7 L/m³.

which is equivalent to a NO removal efficiency of 40%. If the droplet size is reduced from 2 to 1.5 mm, then a increases from 15 to 35 ft²/ft³ (4.6−10.7 m²/m³), and the NTU becomes 1.17, which corresponds to a removal efficiency of 69%. A further reduction of the droplet size would further increase the removal efficiency of NO. However, if the droplet size is too small, many of droplets would be carried up with the flue gas in a counter-current absorber, resulting in entrainment of the liquor.

Regeneration of Iron Chelates. After NO is absorbed, the iron(II)(DMPS)$_2$NO product must be regenerated to iron(II)(DMPS)$_2$ for re-use. In an actual flue gas system with about 5% residual oxygen, some of the iron(II)(DMPS)$_2$ complex will be oxidized, as shown in reactions 2 and 3. DMPS reduces the ferric ion in the oxidized complex back to ferrous ion while the -SH group in DMPS is oxidized, leading to a disulfide (S−S) linkage. Basically, there are two steps involved in the regeneration of iron(II)(DMPS)$_2$: (1) removal of the bound NO and (2) cleavage of the S−S linkage in the oxidized chelate to re-form reduced DMPS. For commercial applications, a simple, efficient, and cost-effective method for regeneration is needed. Several metals were tested as reducing agents for this system.

Initially, batch reduction studies of ferrous nitrosyl solutions were performed. We found that iron metal can rapidly reduce NO bound to ferrous ion complexes to ammonium ion. The overall reduction reaction is shown in reaction 4. The reaction appears to occur on the surface of the iron metal and is believed to proceed via electron transfer from the metal surface to the nitrosyl. There are several forms of metal that can be used, such as powder, filings, or chips. The reduction process is dependent on a number of parameters, including reaction time, pH,

temperature, reactant concentration, metal surface area, and degree of agitation. Since the reaction is heterogeneous, it is dependent on the contact between the iron particles and the solution. The reaction was monitored by observing either the rate of ferrous ion formation (by 1,10-phenanthroline colorimetry) or the rate of NH_4^+ formation (by ion chromatography). The measurement methods were reasonably consistent with one another, and the rate of ferrous ion formation was 2.5 times the rate of ammonium ion formation when both were measured, as would be expected from the stoichiometry of reaction 4. At room temperature, a solution of 10 mM iron(II)(DMPS)$_2$NO at pH 5 was rapidly mixed with iron metal. The mixture was found to have an initial reaction rate of 2×10^{-3} M/min for NH_4^+ production. With less efficient mixing, the initial reaction rate was more than 1 order magnitude slower. Our experiments also indicate that the ligand used in the system also influences the rate of reduction. The reduction of iron(II)(EDTA)NO is significantly faster than reduction of iron(II)(DMPS)$_2$NO under identical reaction conditions.

Batch studies with solutions of oxidized DMPS alone showed that iron metal can also effectively reduce the disulfide bond. The reaction is also heterogeneous, and the overall process is shown in reaction 5. In mixtures of iron metal with oxidized DMPS solutions, the rate of reduction could be monitored by the formation of reduced DMPS, using Raman spectroscopy to follow the increase of the 2578 cm^{-1} -SH band, although it was simpler to determine the rate of ferrous ion formation using colorimetry. The same parameters described above also influence the reduction of oxidized DMPS. The pH of the reaction mixture increases with time, as would be expected from reaction 5. The reaction appears to be somewhat slower than the reduction of the ferrous nitrosyl complex under equivalent conditions.

In further batch experiments, 150 mL of fresh 10 mM iron chelate was placed in a 4.5 cm diameter bubble column and saturated with a flow of 500 ppm NO in nitrogen. The solution was then stirred rapidly with 3 g of iron powder. The pH of the solution rose as the reaction proceeded due to the consumption of hydrogen ion in the reduction shown in reaction 4. The pH increased rapidly in the first minute of the reaction. Small amounts of sulfuric acid or other acids were added to maintain a suitable pH. The regeneration reaction appears to proceed almost to completion within a few minutes. The regenerated iron chelate solution was transferred into the bubble column and was found to absorb substantial amounts of additional NO. In the absence of oxygen, up to 90% of 10 mM iron(II)(DMPS)$_2$NO solution could be regenerated in 5 min by mixing with excess iron powder at 55 °C and pH 4.0–4.5.

The reduction processes were also studied with iron chips instead of iron powder. Iron chips are easier to handle, less expensive, and more suitable for flow systems than iron powder, although they have less surface area per unit weight. It was found that recirculating an iron(II)-(DMPS)$_2$ solution saturated with NO and oxidized with oxygen through a column containing iron chips was an effective way to obtain suitable contact time and metal surface area. Tests of the effects of system parameters were conducted by circulating batches of iron(II)(DMPS)$_2$NO solutions through a small column of iron chips and measuring the amount of NO that could be absorbed following regeneration. It was found that increasing the column temperature, increasing the regeneration time, and
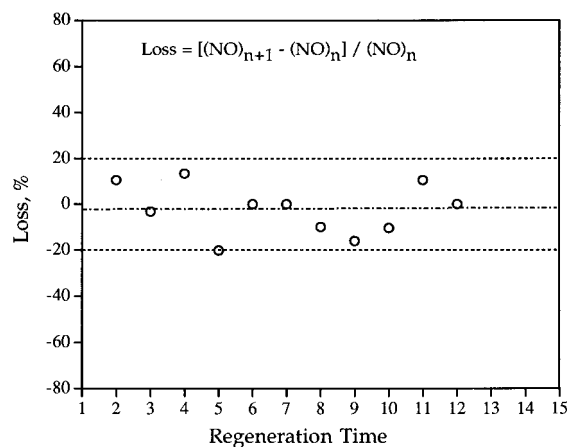

FIGURE 3. Degradation of iron(II)(DMPS)$_2$ solution as a result of regeneration by iron metal and precipitation of excess iron.

lowering the solution pH all increased the observed rate of reduction. Oxygen was included in some studies to generate oxidized DMPS. Up to 67% of an iron(II)(DMPS)$_2$ solution saturated with NO in the presence of 5% oxygen could be regenerated by circulating it through a column of iron chips at 40 °C for 5 min at pH 4–5. Since the solid iron surface area was not well known and the rate of regeneration decreased with time, no attempt was made to determine reaction rates for the reduction processes.

The excess iron in solution produced by the reduction processes must be removed before the scrubbing solution is re-used. Precipitation of iron hydroxides was found to be the most straightforward method for removal of the excess iron. This approach has been used for removal of soluble iron by the water treatment industry. Iron co-precipitation has been tested by the Electrical Power Research Institute at a pilot plant established for removal of trace elements (such as arsenic, selenium, and beryllium) from waste streams at a coal-fired power plant (10, 11). It appears feasible to incorporate an iron precipitation stage in the regeneration system. After regeneration, the iron-(II)(DMPS)$_2$ solution can be raised to pH 6–7 by adding a Ca(OH)$_2$ slurry. A rust-colored precipitate of iron hydroxides forms almost immediately and is easily removed by filtration. Ammonium ions produced by regeneration can be removed as ammonia by air stripping at pH 8 or above. The pH of the solution can be used to separate the removal of excess iron from the removal of ammonia. The ammonia can be fed into the combustion zone of the boiler for destruction. A batch of iron(II)(DMPS)$_2$ solution was used successfully in the NO absorption–regeneration–iron precipitation cycle more than 20 times without problems. The total amount of NO absorbed by this solution was more than 10 times the amount absorbed by the solution without regeneration.

We also investigated the possibility of loss of the iron-(II)(DMPS)$_2$ complex during absorption–reduction–precipitation cycle. Figure 3 depicts iron(II) chelate loss due to regeneration with iron metal and precipitation of excess ferrous ion. The percent loss is defined by

$$\text{percent loss} = 100 \times [(\text{NO})_{n+1} - (\text{NO})_n]/(\text{NO})_n \quad (8)$$

where $(\text{NO})_n$ is the amount of NO absorbed after nth regeneration cycle, and $(\text{NO})_{n+1}$ is the amount of NO absorbed after $(n + 1)$th regeneration cycle. The measurements were made with 50 mM iron(II)(DMPS)$_2$ at pH 5.5
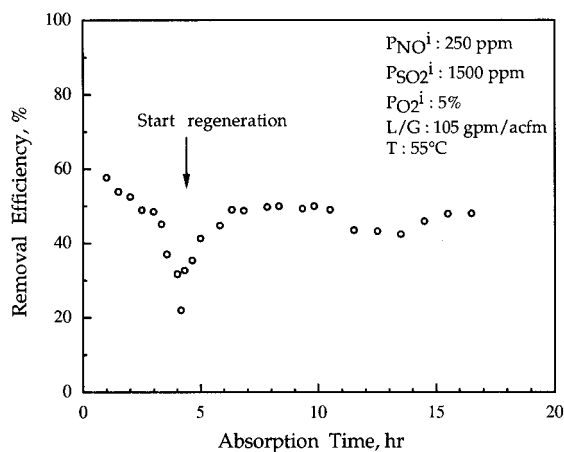
FIGURE 4. NO removal efficiency vs time, showing the effect of regeneration on removal efficiency.

and 55 °C exposed to 500 ppm NO and 5% oxygen. The solution was regenerated for 5 min at pH 4.5 over a temperature range of 33−44 °C. The excess iron was precipitated over a pH range of 6.5−8.2. While there is considerable scatter in the plot, the average loss per regeneration cycle is about 2%. We investigated possible causes of the observed loss. Samples of the scrubbing liquor were collected before and after regeneration for analysis by HPLC. The HPLC analysis showed no evidence of degradation products from the breakdown of DMPS. High pH conditions used for iron hydroxide precipitation may cause some co-precipitation of iron(II)(DMPS)$_2$ along with the iron hydroxides. Loss may also occur as co-precipitation when calcium sulfate precipitates after absorption and oxidation of SO_2. It is desirable to avoid the formation of calcium sulfite, which can entrain significantly more solution than calcium sulfate during precipitation. It will be necessary to determine the most suitable pH for removal of excess iron in this system. While it appears that loss by co-precipitation is more significant than DMPS breakdown during regeneration, neither condition presents an insurmountable problem to the development of the process.

Integrated Tests. The batch system studies were used to plan integrated tests of the new scrubbing system. These tests included the absorption of SO_2 and NO from a gas stream, the removal of solids, the regeneration of iron-(II)(DMPS)$_2$, and the stripping of ammonia. The system consisted of the 10 cm diameter TCA absorber, a holding tank, a thickener, filters, a regeneration reactor, and an air stripper. A steady level of NO removal could be maintained during an entire run, which usually lasted several hours. The NO removal efficiency depends on the amount of liquor diverted for regeneration and the conditions used in the regeneration reactor. Figure 4 shows the effect of operating conditions during a 16.5 h test. The first 4 h were conducted without the regeneration of the liquor, and then the regeneration was started and continued for the rest of the run. This experiment was carried out at 55 °C with 5% oxygen, a L/G of 105 gpm/1000 acfm (14.0 L/m^3), an initial iron(II)(DMPS)$_2$ concentration of 50 mM, and inlet NO and SO_2 concentrations of 250 and 1500 ppm, respectively. The flow rate of scrubbing liquor into the regeneration loop and the absorption loop was 0.05−0.1 gpm (0.19−0.38 L/min) and 1.5 gpm (5.6 L/min), respectively. The system had an initial NO removal efficiency of 60%, which declined to about 20% after 4 h. After activating the regeneration
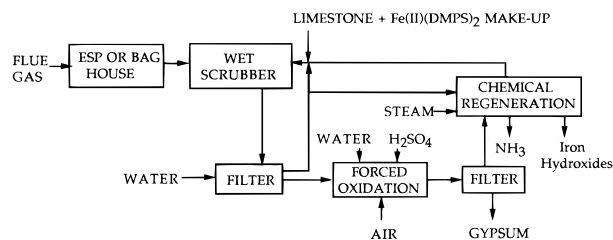

FIGURE 5. Conceptual flow diagram of an integrated limestone/iron(II)(DMPS)$_2$ system for combined removal of SO_2 and NO_x from flue gas.

system, the NO removal efficiency increased and stabilized at a level between 43 and 51%. The removal efficiency depended on the operating conditions employed in the regeneration system. These tests show that the regeneration method works effectively. We believe that further improvement of the NO removal efficiency could be achieved by increasing liquor diverted for regeneration, increasing the regeneration time and/or temperature, properly controlling the liquor pH during regeneration, and improving the contact between the liquor and the iron chips.

For combined removal of NO_x and SO_2 in a commercial wet FGD system, the reagent loss due to liquor entrainment in solids must be addressed. If we assume that an average loss rate of DMPS is about 2%, then the DMPS loss would be about 4 short tons per day in a typical wet limestone FGD system. We believe that by optimizing regeneration conditions, the loss of DMPS during regeneration and removal of excess iron can be kept below 1%. This would keep DMPS loss per day below 2 tons in a full-scale FGD system. This loss could be further reduced by washing the iron hydroxide solid from the regeneration system to recover DMPS.

Solid precipitates from a wet limestone FGD system using unforced oxidation may occlude as much as 50% by weight of liquor and contribute to significant loss of reagents. If a wet limestone scrubber with 10 mM iron(II)(DMPS)$_2$ removed 90% of SO_2 from a 500 MW coal-fired power plant generating flue gas with 2000 ppm SO_2, it would consume about 2.7 short tons of DMPS per day due to entrainment. This loss could be reduced by washing the filter cake to recover the reagent. Under forced oxidation conditions, the reagent loss due to entrainment is only one-fifth that under the unforced oxidation conditions. This is because the gypsum precipitate formed under forced oxidation occludes only 10% by weight of the liquor. However, aeration under forced oxidation would also increase the oxidation of iron(II)(DMPS)$_2$. To circumvent this problem, the forced oxidation aeration could be performed after the extraction of the entrained liquors. Figure 5 depicts the flow diagram of such a process, which includes extraction of entrained liquor from the solid to recover the reagent, followed by the forced oxidation to produce gypsum. The scrubbing liquor is subsequently regenerated by the chemical reduction method described here.

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