

The Potential of a Wet Process for Simultaneous Control of SO_2 and NO_x in Flue Gas[†]

S. G. Chang* and D. Littlejohn

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Power plants release oxides of sulfur and nitrogen into the air as a result of the burning of fossil fuels. At high concentration these gases directly affect human health, and when further oxidized and hydrolyzed, they are converted into sulfuric and nitric acids and fall to earth as acid rain to corrode metals and etch buildings and monuments made of calcareous rock. Acid rain will also acidify surface and ground water to a point where toxic trace metals reach concentrations that make the water unfit for human consumption or unsuitable for aquatic animals, and inhibit crop and forest productivity. Therefore, oxides of sulfur and nitrogen in power plant flue gas should be removed before they are released to the atmosphere.

While the development of flue gas clean-up processes has been progressing for many years, a satisfactory process is not yet available. Lime/limestone wet flue gas desulfurization scrubber is the most widely used process in the utility industry at present. The wide use of this type of process is due primarily to the fact that these processes are the most technically advanced and generally the most economically attractive. In spite of this, it is expensive and accounts for about 25-35% of the capital and operating costs of a power plant. Techniques for the control of nitrogen oxides emissions in the post combustion have not been developed as extensively as those for control of sulfur dioxide emissions. Several approaches have been proposed. Among these, ammonia-based selective catalytic reduction (SCR) has received the most attention. But, SCR may not be suitable for U.S. coal-fired power plants because of reliability concerns and other unresolved technical issues. These include uncertain catalyst life, water disposal requirements, and the effects of ammonia by-products on plant components downstream from the reactor. The sensitivity of SCR processes to the cost of NH_3 is also the subject of some concern.

The development of a process that is simple and can allow an efficient removal of both SO_2 and NO_x simultaneously in one system could provide economical advantage. In the 70's, Japanese pursued this approach and developed several types of wet flue gas simultaneous desulfurization and denitrification processes which were demonstrated to be highly efficient in SO_2 and NO_x removal (about 90% for NO_x and 99% for SO_2). However, these wet processes have not reached the commercial stage yet because they are uncompetitive economically, according to cost evaluation. These cost evaluations, however, were made based on design and knowledge available at that time. Critiques have indicated that these wet processes are in their early stages of development and with their maturation, they could become competitive in cost.

The most promising type of wet process developed so far, such as Asahi process, is based on the addition of ferrous chelates in scrubbing liquor to enhance the absorption of NO by forming ferrous nitrosyl chelates in aqueous solutions. Ferrous nitrosyl chelate can then react with dissolved SO_2 to produce N_2 , N_2O

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dithionate, sulfate and various N-S compounds, while some ferrous chelate is oxidized to ferric chelates, which are inactive. Therefore, this type of process requires regeneration of scrubbing liquors by removing dithionate, sulfate, and N-S compounds from the solutions and reduction of ferric chelate back to ferrous chelates. The chemistry of this type of process is complicated and has not been well investigated. Therefore, an optimum design of a system of this type can not be achieved. This paper discusses some important factors that should be considered in identifying an optimum metal chelate catalyst and in developing an efficient scrubber for the simultaneous desulfurization and denitrification of a power plant stack gas. The kinetics and products of the reaction of ferrous nitrosyl chelates with aqueous SO_2 have been investigated. The effect of this reaction on scrubber operation is also discussed.

Thermodynamic Equilibrium and Kinetics of NO and SO_2 Absorption

The solubility of NO in aqueous solutions is very small. The solubility coefficients is 1.93×10^{-3} mol/L-atm at 25° C and zero ionic strength (μ). The solubility decreases with increasing temperature; the enthalpy of solution is $\Delta H = -2.94$ Kcal/mol. The solubility of NO decreases with increasing ionic strength; this decrease amounts to approximately 8% for $\mu = 0.1$ mol/L. The solubility of NO in aqueous solution was found to be independent of pH over the range 2-13. For 1000 ppm of NO in equilibrium with aqueous scrubbing solution at 50° C and $\mu = 0.1$ mol/L, the concentration of NO in the aqueous phase is only 1.2×10^{-6} mol/L. The absorption of NO is enhanced by some water-soluble metal chelate compounds which forms complexes with NO. We have determined the equilibrium constants, enthalpy, and entropy for the coordination of NO to several ferrous chelates using a laboratory scale gas absorption apparatus and a temperature-jump apparatus. For an aqueous scrubbing solution initially containing 0.1 mol/L $Fe^{2+}(NTA)$ at 50° C, $\mu = 0.1$ mol/L, the fraction of the iron chelate that is converted to $Fe^{2+}(NTA)NO$ is about 36% when the solution is in equilibrium with a gas containing 1000 ppm of NO at 1 atm. Thus, the presence of the $Fe^{2+}(NTA)$ increases the capacity of the scrubbing solutions of NO by a factor of 30,000 or more.

With the temperature-jump technique, we have directly measured the formation and dissociation rate constants of several ferrous nitrosyl chelates. For both $Fe^{2+}(EDTA)NO$ and $Fe^{2+}(NTA)NO$, the relaxation times due to the temperature jump were too fast to be measured. However, an upper limit of 10 μ s was established for the relaxation times for both complexes.

Sulfur dioxide is moderately soluble in water. The solubility coefficient of SO_2 is 1.24 mol/L-atm at 25° C. Hydrated SO_2 can ionize to form bisulfite and sulfite ions. The equilibrium constants of these ionizations are known. The equilibrium concentrations of total aqueous S(IV) species increases with increasing solutions pH at a given partial pressure of SO_2 . The rate constants of ionization of hydrated SO_2 has been measured to be very fast (3.4×10^6 sec⁻¹ at 20° C) by Eigen et al. by using a relaxation technique.

Reaction of $Fe^{2+}(L)NO + SO_3 = HSO_3^-$

A number of studies have been made of the reaction of ferrous nitrosyl chelates with sulfite and bisulfite ion in recent years. Reports of the reaction have indicated that it is complicated, and have not provided a complete understanding of the reaction mechanisms. There are contradictions in the literature as to what the reaction products are, as well as the kinetic behavior. We have recently studied the reaction using several different analytical techniques. The observed reaction products are Fe(III), SO_4^{2-} , $S_2O_6^{2-}$, N_2 , N_2O , and N-S compounds.

Gaseous products were analyzed by an Aerograph A700 gas chromatograph with a Porapak Q column. SF_6 was used over most solutions and as a carrier gas to allow determination of N_2 generated by the reaction mixtures. Occasionally, gas samples were withdrawn and run on an A.E.I. MS12 mass spectrometer to check the results obtained by gas chromatography.

Ferrous ion concentrations were determined by the 1,10 phenanthroline method. Test solutions were acidified to pH \sim 2.5 to avoid interference from the ligands used in the reaction mixtures.

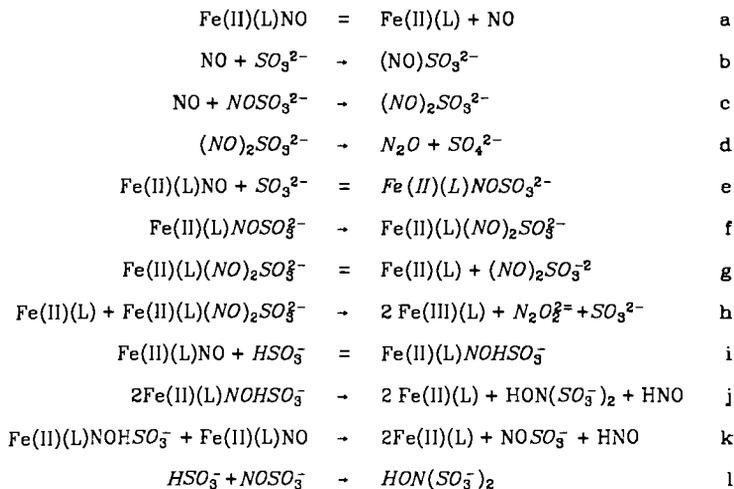
We have developed a laser Raman spectroscopic and ion chromatographic techniques that can be successfully used in the determinations of N-S compounds in reaction mixtures. Both techniques require only a small amount of the sample and allow simple, rapid and simultaneous determination of these compounds. Figure 1 shows Raman spectra of the N-S compounds along with the sulfate ion reference peak at 980 cm^{-1} . The spectra can be quantified by adding a known amount of a reference compound, such as ClO_4^- , to the sample and comparing peak heights. The peak heights must be corrected for the relative scattering efficiencies of the compounds (Table 1). Using a Dionex 2010i Ion Chromatograph with a conductivity detector, we can make determinations of N-S compounds. Figure 2 shows composite ion chromatogram of the N-S compounds.

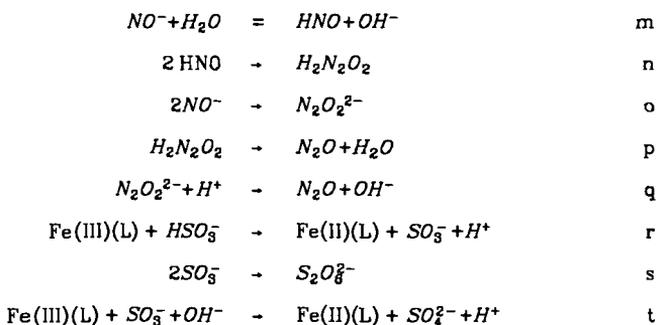
The kinetics of the disappearance of the ferrous nitrosyl complex was monitored by observing one of the visible absorption bands of the complex with a Cary 219 spectrophotometer interfaced to an Apple II+ computer. The rate expression we obtained is:

$$\frac{d[Fe(II)(L)NO]}{dt} = k_1[HSO_3^-] + k_2[SO_3^{2-}][Fe(II)(L)NO] \quad 1)$$

For L = EDTA at 55° C and pH 4 to 8, $k_1 = 9.0 \times 10^{-5}\text{ sec}^{-1}$ and $k_2 = 0.60\text{ M}^{-1}\text{ sec}^{-1}$. These values are valid for $10^{-4}\text{ M} < [Fe(II)(EDTA)NO] < 10^{-3}\text{ M}$ and $10^{-3}\text{ M} < [S(IV)] < 10^{-1}\text{ M}$.

From the reaction products observed and their behavior, we have developed the following reaction mechanism:





This mechanism provides an explanation of the complexity of this reaction system and helps explain the results obtained by others.

Regeneration of Scrubbing Liquors

The scrubbing liquors leaving an absorber must be regenerated before being recycled back to the absorber. Ferric chelates, produced as a result of the oxidation of ferrous chelate catalysts by residual oxygen in flue gas and ONNOSO_3^- in the system, are inactive and must be reduced back to ferrous chelates. It is known that ferric ion can react with bisulfite ion to form ferrous ion and dithionate (r and s). This reduction method has been employed in the Asahi process. Also the sulfate, dithionate, and N-S compounds produced from the reaction of ferrous nitrososulfonates and ferrous nitrosyl chelates (j, k and l) in the scrubbing liquors must be removed to prevent its buildup in the scrubbing solutions.

In the Asahi process, the flue gas enters a packed-bed absorber where it flows countercurrent to a 6.3 pH sodium-salt scrubbing solution containing Fe^{2+} (EDTA). The liquid effluent from the absorber is then pumped to a reducing tank. Most of the scrubbing liquors leaving the reducing tank is recycled to the absorber. Only about 10-20% of liquors is pumped to an evaporator system in the regeneration section. The concentrated solution from the evaporators is then pumped to a cooling crystallizer where hydrated sodium dithionate and sulfate crystals are produced under vacuum. These crystals are separated from the mother liquor in a screw decanter and sent to a dryer operating at 250° F-300° F in which the hydrated crystals are converted to anhydrous sodium salts. Most of the mother liquor from the decanter is recycled to the reducing tank and a smaller stream is passed through a N-S compounds treatment section. The N-S compounds are converted to relatively insoluble potassium salts by reaction with potassium sulfate. The potassium salts of N-S compounds are separated in a screw decanter and sent to a thermal cracker for the decomposition at about 930° F.

The high capital investment cost of the Asahi process is due to the necessity for large absorbers, evaporators, crystallizers, dryers, rotary kiln crackers and screw decanter separators. The major operating and maintenance costs are electricity, fuel oil, steam and chemicals such as soda ash, EDTA and limestone. The requirement for consumption of large amount of utilities is associated with the operation principle and design of the Asahi process.

Further research areas where improvement of this type of process such as the Asahi process might be made to provide economic advantage will be discussed.

Table 1

Species	Raman Shift (cm^{-1})	Relative Molar Intensity ^a
NO	1877	-
N ₂ O	1285	-0.18
NO ₂ ⁻	818	0.053
	1240	-0.025
	1331	0.125
NO ₃ ⁻	1050	0.95
N ₂ O ₂ ²⁻	892 ^b	weak ^b
	1115 ^b	weak ^b
	1383 ^b	strong ^b
SO ₃ ²⁻	967	0.12
HSO ₃ ⁻	1023	-0.10
	1055	-0.13
SO ₂ ·H ₂ O	1152	-
S ₂ O ₆ ²⁻	710	0.47
	1092	1.48
SO ₄ ²⁻	455	-0.07
	961	1.00
HSO ₄ ⁻	1050	0.05
(NO) ₂ SO ₃ ²⁻	932	0.19
	1051	0.31
	1130	0.51
HADS	700	0.13
	1084	1.43
HAMS	760	0.075
	1058	0.48
ATS	1097	1.80
ADS	1084	1.02
HA (pH 7)	1004	0.21
HA (pH 9)	818	0.09
SA (pH 3)	1049	0.41
H ₃ BO ₃	878	0.22

a. SO_4^{2-} 961 cm^{-1} = 1.000

b. J. E. Rauch and J. C. Decius, Spectrochim. Acta 22, 1963 (1966)

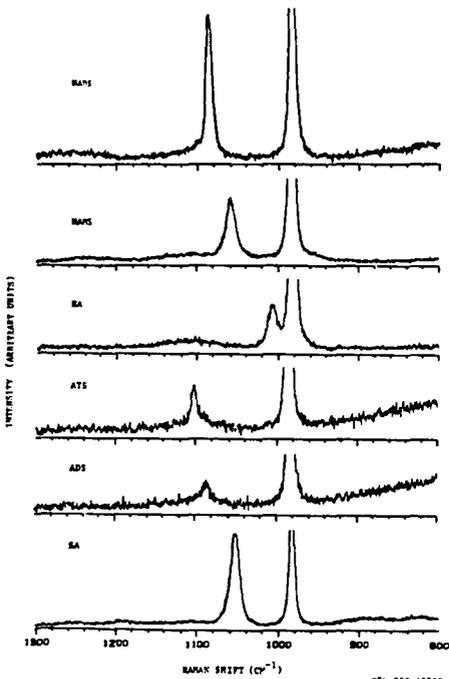


Figure 1 Raman spectra of (from top to bottom) HADS, HAMS, HA, ATS, ADS, and SA, along with SO_4 reference peak at 980 cm^{-1} .

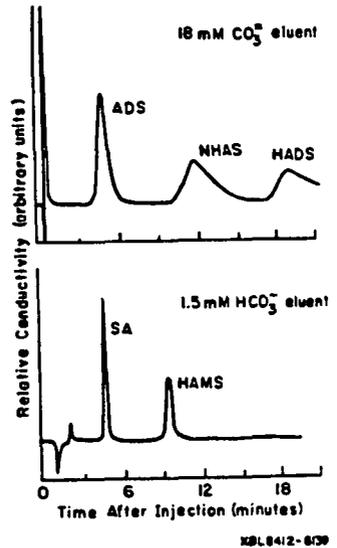


Figure 2 Ion chromatograms of ADS and HADS with 18 mM CO_3 eluent (upper trace) and SA and HAMS with 1.5 mM HCO_3 eluent (lower trace).