

SULFUR TRIOXIDE FORMATION IN THE PRESENCE OF
RESIDUAL OIL ASH DEPOSITS IN AN ELECTRIC UTILITY BOILER

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A model is proposed for the catalytic oxidation of sulfur dioxide to sulfur trioxide over vanadium-containing ash deposits on heat exchanger tubes in the convective section of a residual oil-fired boiler. The model includes a global description of the rates of forward and reverse reactions at the deposit surface and mass transfer of the product SO_3 from the deposit surface to free stream. The kinetic parameters for the chemical reaction and the ratio of active deposit surface area to geometric external area are the principal adjustable parameters. Conversion of SO_2 to SO_3 is strongly dependent on the surface area-temperature-residence time distribution in the convective section. The change in surface temperature with increasing deposit thickness accounts for a significant part of the increase in sulfur trioxide content of stack gas which occurs as ash accumulates on convective tubes.

INTRODUCTION

A few percent of the sulfur in residual fuel oil typically appears as sulfur trioxide in the stack gas from an electric utility boiler. Sulfur trioxide is completely converted to sulfuric acid vapor at approximately 500 K (440°F), and condenses as aqueous sulfuric acid at the dewpoint, near 400 K (260°F) (Halstead and Talbot, 1980). Adsorption of the acid on unburned coke particles and reaction with ash increases the particulate matter concentration in the combustion products, when measured by USEPA Method 5. Acid droplets contribute to the visual opacity of the stack plume. The distribution of sulfur oxides among gaseous species, droplets, and particles influences the dispersion, atmospheric reactions, and deposition of sulfate from the plume.

Vanadium, one of the most abundant inorganic impurities in many residual fuel oils, is the active ingredient of commercial catalysts for oxidation of sulfur dioxide to sulfur trioxide in the manufacture of sulfuric acid. The fraction of sulfur oxides emitted as sulfur trioxide from an oil-fired boiler has been observed to increase with increasing vanadium content of the fuel, with increasing excess oxygen in the flue gas, and with accumulation of vanadium-containing deposits on heat exchanger tubes. In the present paper we examine the effect of the deposit surface temperature on sulfur trioxide formation.

Reactions determining the formation and fate of SO_3 in oil-fired boilers are shown as functions of temperature in Figure 1. In the flame and postflame regions, above about 1200 K (1700°F), the steady-state concentration of SO_3 is approximately described by formation and destruction reactions of SO_2 and SO_3 with oxygen atoms (Merryman and Levy, 1971). Detailed discussions of the homogeneous reaction system are given by Cullis and Mulcahy (1972) and by Smith, Wang, Tseregounis, and

Westbrook (1983). The equilibrium distribution of sulfur oxides shifts toward SO₃ as temperature decreases, so the concentration of SO₃ just downstream from the furnace exit is determined by the relative rates of the formation reactions and cooling of the combustion products in this region. Typically 1 mol% of the sulfur oxides are thought to be present as SO₃ in furnace exit gas, i.e. on the order of 10 mol ppm in the products from combustion of 2 wt% sulfur oil. If SO₃ remained at this level, low temperature corrosion, plume opacity, and other problems associated with sulfuric acid would not be too troublesome.

Oxidation of SO₂ is catalyzed by iron- and vanadium-containing ash deposits in the convective section of a boiler. Conversion of SO₂ to SO₃ via heterogeneous reactions is greatest over a relatively narrow temperature range, from about 780 to 980 K (950 to 1300°F) (Wickert, 1963; Reid, 1971). At lower temperatures, formation of SO₃ is limited by the rate of the surface reaction; at higher temperatures it is limited by the equilibrium distribution of sulfur oxides, which increasingly favors the reactants, O₂ and SO₂, as temperature increases. When the heterogeneous contribution to SO₃ formation is significant, problems associated with sulfate and sulfuric acid are more severe. Plume visibility due to acid mist increases as ash deposits accumulate (Reidick and Riefenhäuser, 1980). A model for SO₃ formation in boilers, including both homogeneous and heterogeneous reactions, was developed by Squires (1982). Release of SO₃ accumulated in ash deposits during operation at reduced load was proposed by Shareef, Ramsay, and Homolya (1986) and Shareef, Homolya, and Mormile (1990) to explain the increase in plume opacity associated with increase in load, following a period of low-load operation.

The formation of sulfuric acid vapor and liquid is shown at the bottom left in Figure 1. All four of the major sulfur-containing species, gaseous SO₂ and SO₃, as well as liquid and vapor phase H₂SO₄, may react with metal oxides in the oil ash forming metal sulfates, processes which are shown at the bottom right in Figure 1. Little is known about the relative importance of these reactions, or the relative amounts of sulfate present in particulate matter as metal salts and adsorbed sulfuric acid (Halstead, 1978; Penfold and Smith, 1982). A conservative estimate of the contribution of sulfate to particulate matter would require that one place all of the SO₃ in the particulate, but a conservative estimate of the contribution of acid droplets to opacity would require one to assume that all of the SO₃ forms sulfuric acid mist! More experimental work on the distribution of these species is needed.

MODEL FOR CATALYTIC SO₃ FORMATION

The model is based on the assumption that only ash deposited on convective tubes contributes to SO₃ formation, according to the overall reaction



Ash particles suspended in the gas stream are neglected because their external surface area per unit of flue gas volume is much smaller than that of deposits. Some SO₃ is considered to be present in the gas entering the convective section, but flame and postflame homogeneous reactions are not included in the simulation.

The kinetics of heterogeneous oxidation of SO₂ were reviewed by Urbanek and Trela (1980). A global expression for the rate of formation of SO₃, assuming a rate proportional to the mass fraction of vanadium oxides in deposits, is

$$r_{\text{SO}_3} = k Y_{\text{VO}_x} S_d C_{\text{O}_2}^a C_{\text{SO}_2}^b \left[1 - \frac{C_{\text{SO}_3, s}}{K C_{\text{SO}_2} C_{\text{O}_2}^{1/2}} \right] \quad (2)$$

The factor in brackets accounts for the approach of the rate to zero as the SO₂ concentration adjacent to the catalyst surface approaches its equilibrium value. Under conditions of interest in boilers the extent of reaction is small, so changes in the SO₂ and O₂ concentrations are negligible. When the system is steady, the rate of SO₂ formation at the deposit surface equals its rate of transport from the surface to the free stream:

$$r_{SO_2} = \frac{Sh_t D_{SO_2}}{d_t} A_t (C_{SO_2,s} - C_{SO_2}) \quad (3)$$

Elimination of the unknown concentration at the surface and integration over time, with the boundary condition, C_{SO₂} = C_{SO₂,o} at t = 0, gives:

$$C_{SO_2} = K C_{O_2}^{1/2} C_{SO_2} + [C_{SO_2,o} - K C_{O_2}^{1/2} C_{SO_2}] \exp(-k' A_t t) \quad (4)$$

C_{SO₂,o} and C_{SO₂} are the SO₂ concentrations entering and leaving, respectively, a region in which deposit surface temperature and composition are approximately constant. The effective rate coefficient, k', is given by:

$$\frac{1}{k'} = \frac{1}{Sh_t D_{SO_2}} + \frac{1}{\frac{k S_d}{K A_t} Y_{VOx} C_{O_2}^{a-1/2} C_{SO_2}^{b-1}} \quad (5)$$

The kinetic parameters were estimated from the work of Glueck and Kenney (1968), who observed that the reaction over a vanadium oxide-potassium oxide melt was first order in SO₂ (b = 1), and zeroth order in O₂ (a = 0). After choosing the kinetic constants, the most important adjustable parameter in the model is the ratio of effective catalytic surface area to the geometric external surface area of deposits, S_d/A_t.

RESULTS

A study of SO₂ formation was conducted by the Consolidated Edison Co. of New York at Arthur Kill Station (Piper and Kokoska, 1983; Shareef, Ramsay, and Homolya, 1986; Shareef, Homolya, and Mormile, 1990). The majority of testing was conducted on the superheat furnace of Arthur Kill Unit 20. This unit normally fires oil containing less than 0.3 wt% sulfur, but the testing for the SO₂ study was performed using oil containing 0.75 wt% sulfur. Measurements of SO₂ were made as functions of load during both transient and steady-state operation. Under steady full load conditions, the level of SO₂ in flue gas varied between 31 and 40 mol ppm over three days of tests. Gas temperatures, tube temperatures, gas velocities, and residence times were calculated for 14 separate tube bundles from the platen superheater inlet to economizer outlet (Piper and Kokoska, 1983; Piper, 1985).

The model described above was used to examine the influence of deposit accumulation on SO₂ formation, considering only the effect of deposit thickness on the surface temperature distribution, neglecting any change in the effective surface area of catalyst which might be associated with deposit growth. The increase in surface temperature with increasing deposit thickness was estimated by assuming that deposit was built on surfaces whose temperatures were fixed at the values calculated by Piper (1985). The deposition rate was assumed to be 1 g/m²-hour, distributed uniformly over the length and circumference of the tubes. Changes in deposition rate with changes in gas, tube, and surface temperatures were not considered. Equation 4 was applied to successive banks of convective tubes, from the furnace exit to economizer outlet. The calculated SO₂ profiles through the convective section after 0, 3, 6, and 12 months of continuous full load

operation are shown in Figure 2. Position in the convective passage is given as a fraction of the total gas residence time. The surface temperature distribution calculated by Piper (1985) is the base case, shown at the bottom of the figure. The calculated thickness of deposits after 12 months of continuous full load operation was 4 mm.

Under the conditions investigated, the temperature distribution is such that the rate of heterogeneous SO_3 formation is low near the entrance to the convective section, then increases, and decreases as the combustion products move downstream. The model properly accounts for the observation that the rate of SO_3 formation peaks in a narrow temperature window, the actual range of temperatures depending on conditions such as mass transfer between the free stream and catalyst surface, concentrations of O_2 and SO_2 , etc. As ash thickness and surface temperature increase, the activity of deposits near the entrance to the convective section decreases as their temperatures move farther from the optimum range. However, the decrease in SO_3 formation rate at the entrance is more than compensated by an increase in rate in the larger surface area, higher gas velocity tube banks in the middle of the convective section, with the result that SO_3 continuously increases with increasing fouling of the tubes. For the assumed conditions, SO_3 at the economizer outlet (far right) increases from 33 to 44 mol ppm over the 12 month period. Changes in surface temperature distribution may therefore be a significant factor in the increase in sulfate emissions with time after cleaning of a unit, apart from any effect of an increase in effective surface area of deposits.

CONCLUSION

Simulation of the catalytic oxidation of SO_2 to SO_3 over vanadium-containing ash deposits, including chemical reaction between SO_2 and O_2 at the surface and diffusion of SO_3 from the surface to free stream, shows that changes in deposit surface temperature associated with deposit growth may be a significant influence on SO_3 formation. Using conditions in Arthur Kill Unit 20 as a baseline, and assuming deposit growth at the rate of $1 \text{ g/m}^2\text{-hour}$ while firing 0.75 wt% sulfur oil, changes in deposit surface temperature resulting from the increase in deposit thickness were estimated to cause a 30% increase in SO_3 at the economizer outlet over a period of 12 months at full load.

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NOMENCLATURE

- a order of the heterogeneous reaction with respect to O_2 , dimensionless
- A_c geometric external surface area of tubes or deposits, per unit of gas volume, m^{-1}
- b order of the heterogeneous reaction with respect to SO_2 , dimensionless
- C_i concentration of species i , kmol/m^3

- d_t tube diameter, m
- D_{SO_2} molecular diffusion coefficient of SO_2 in combustion products, m^2/s
- k rate coefficient for the heterogeneous reaction between SO_2 and O_2 , the dimensions depend upon the orders of reaction, a and b
- k' effective rate coefficient for SO_3 formation, including surface reaction and boundary layer diffusion, m/s
- K equilibrium constant, in terms of concentrations, for the reaction $SO_2 + 1/2 O_2 = SO_3$, $m^{3/2}/kmol^{1/2}$
- r_{SO_3} rate of sulfur trioxide formation, $kmol/m^3 \cdot s$
- S_d effective surface area of catalytic deposits per unit of gas volume, m^{-1}
- Sh_t average Sherwood number for mass transfer between tube or deposit surface and free stream, dimensionless
- t time, s
- Y_{Vx} mass fraction of vanadium oxides in deposits, dimensionless

Subscripts

- o initial value
- s condition at the catalytic deposit surface

REFERENCES

- C. F. Cullis and M. F. R. Mulcahy, The Kinetics of Combustion of Gaseous Sulphur Compounds, *Combustion and Flame* **18** (1972) 225-292.
- A. R. Glueck and C. N. Kenney, The Kinetics of the Oxidation of Sulfur Dioxide over Molten Salts, *Chemical Engineering Science* **23** (1968) 1257.
- W. D. Halstead, The Nature of H_2SO_4 in Deposits of Acid Contaminated Combustion Grits, *Journal of the Institute of Fuel* **51** (1978) 149-153.
- W. D. Halstead and J. R. W. Talbot, The Sulphuric Acid Dewpoint in Power Station Flue Gases, *Journal of the Institute of Energy* **53** (1980) 142-145.
- E. L. Merryman and A. Levy, Sulfur Trioxide Flame Chemistry - H_2S and COS Flames, Thirteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1971, pp. 427-436.
- D. Penfold and A. C. Smith, The Analysis of Carbonaceous Material from Oil-Fired Boilers, *Journal of the Institute of Energy* **55** (1982) 98-101.
- B. Piper, 1985, Arthur Kill 20 SO_3 Model, Appendix B to Shareef, Ramsay, and Homolya, (1986).
- B. Piper and T. Kokoska, Opacity Study - Data to Support SO_3 Formation Analysis, KVB 81-21620-1447, Report prepared by KVB, Inc., for the Consolidated Edison Co. of New York, Inc., 1983.

W. T. Reid, External Corrosion and Deposits, Boilers and Gas Turbines, American Elsevier, New York, 1971, pp. 75-114.

H. Reidick and R. Reifenhäuser, Catalytic SO₃ Formation as Function of Boiler Fouling, *Combustion*, Vol. 51, No. 8, February 1980, pp. 17-21.

G. S. Shareef, J. B. Homolya, and D. J. Mormile, SO₃ Formation over Fuel Oil Fly Ash Deposits, 1990 SO₂ Control Symposium, New Orleans, LA, May 8-11, 1990.

G. S. Shareef, G. G. Ramsay, and J. B. Homolya, Development and Calibration of a Prediction Model for the Formation of Sulfur Trioxide in a Residual Oil-Fired Boiler, Report prepared for the Consolidated Edison Co. of New York, Inc., by Radian Corp., Research Triangle Park, NC, 1986.

O. I. Smith, S.-N. Wang, S. Tseregounis, and C. K. Westbrook, The Sulfur Catalyzed Recombination of Atomic Oxygen in a CO/O₂/Ar Flame, *Combustion Science and Technology* 30 (1983) 241-271.

R. T. Squires, The Kinetics of SO₃ Formation in Oil-Fired Boilers, *Journal of the Institute of Energy* 55 (1982) 41-46.

A. Urbanek and M. Trela, Catalytic Oxidation of Sulfur Dioxide, *Catalysis Reviews, Science and Engineering* 21 (1980) 73-133.

K. Wickert, The Oil-Firing Yearbook, Kopf, Stuttgart, 1963.

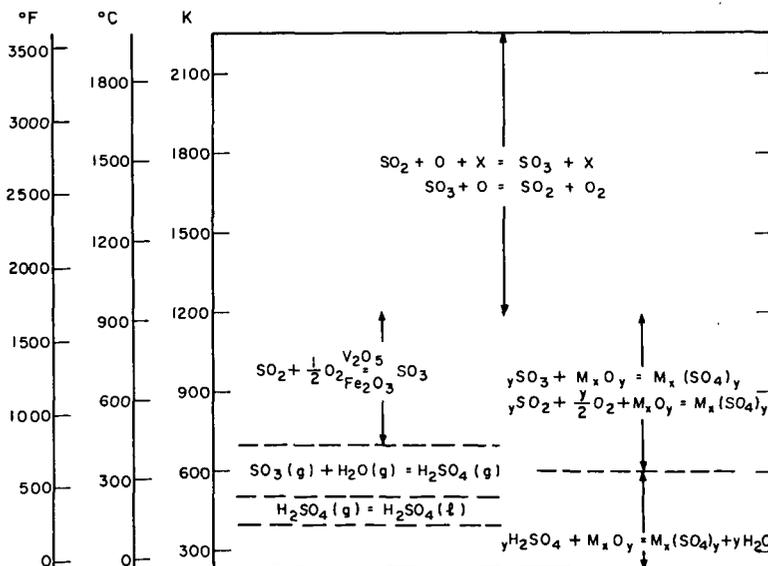


Figure 1. Processes contributing to formation of sulfur trioxide, sulfuric acid, and sulfates in residual oil-fired boilers.

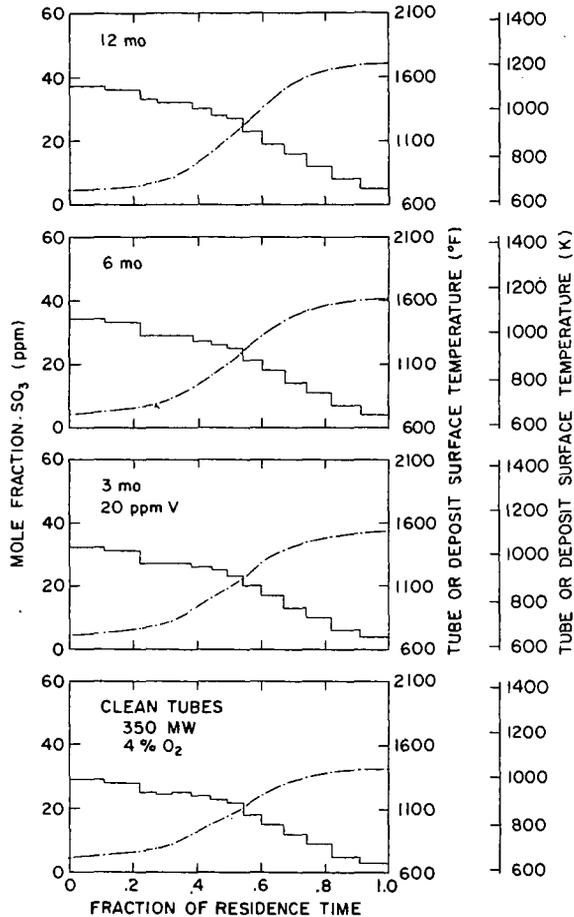


Figure 2. Expected change in SO₃ formation in Arthur Kill Unit 20 as ash deposits accumulate on the convective tubes. Solid line: surface temperature; dot-dash line: SO₃ mole fraction. The estimates are based on the gas temperature-tube temperature-tube area-gas velocity calculations of Piper and Kokoska (1983) and Piper (1985). The fuel oil sulfur content was 0.75 wt%, different from the 0.3 wt% sulfur oil normally fired in the unit. Ash deposits were assumed to grow at the rate of 1 g/m²-hour. As the thickness of deposits increases, the formation of SO₃ decreases at the entrance to the convective section because the equilibrium ratio of SO₃/SO₂ decreases with increasing temperature. However, the ultimate mole fraction of SO₃ at the economizer outlet (far right) increases, because the contribution to SO₃ formation from the higher gas velocity, higher surface area region near the middle of the convective section increases.