Radiation-induced Wet Scavenging of NO_x from Flue Gas

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An improvement in E-beam removal of NO from gas by spraying with alkali solutions is reported, and the scrubbing processes of N_2O_3 and N_2O_4 in aerosol droplets are discussed.

The removal of NO_x from flue gas in a new E-beam clean-up process is a purely radiation-induced process.[1] The energy efficiency of NO oxidation decreases with increase in dose because of back reactions. An increase in removal efficiency of up to 50% by double (or multiple) irradiation, with intermediate product removal, has been demonstrated.[1] This method becomes effective at high doses. It is also attractive to increase energy efficiency at low doses. This may be achieved by the dissolution in aerosol droplets of not only NO_2 but also N_2O_3, N_2O_4 and other nitrogen compounds produced on irradiation. Similar processes have been carried out in the industrial production of nitric acid and are widely considered in cloud-water chemistry. Thus, the main question is: is it possible to achieve radiation-induced wet scavenging processes at low admixture concentrations and short irradiation times.

An aerosol phase in the irradiated gas was created experimentally by spraying water or alkali solutions (the average particle radius was *ca.* 15 μm). The irradiation (Van-de-Graaf electron accelerator, $E_e = 1.8$ MeV, $P_{max} = 200$ W) of the air–aerosol mixture was performed under turbulent conditions created by the kinetic energy of the air–aerosol jet from the sprayer (the ratio of gas–aerosol jet velocity to average gas-flux velocity was *ca.* 10^2). The experiments were conducted in flow stainless steel equipment at atmospheric pressure, $T \approx 330$ K, air flow rate 33 $cm^3\ s^{-1}$ and irradiation time 2.5 s. The initial NO concentration in air was 200–400 ppm and, as has been shown earlier,[2] the rate of NO oxidation was practically independent of its initial concentration. The gas analysis was performed by a spectrophotometer. The average volume dose rates were determined by gas–ethylene dosimetry under flow conditions. The details of the experimental procedure have been described elsewhere.[2]

Fig. 1 demonstrates the dose dependence of specific NO removal (ppm kGy^{-1}) for air mixtures containing water vapour and aerosol. The increase in dose was achieved by the dose rate increasing over the range 0.5–4 kGy s^{-1}. As was shown,[3] the oxidation radiation yield is practically independent of dose rate. The curves 1 (water vapour content ≈20 mass%) and 2 (aerosol volume content $\approx 3 \times 10^{-4}$) correspond to similar water contents. The effect of water aerosol spraying is seen, and becomes apparent particularly at high doses (≥ 5 kGy). This is explained by dissolution of the HNO_3 produced in the gas phase[4] into the aerosol droplets. As has been shown earlier[2] the specific NO removal increases with aerosol volume growth. A comparison of our results and of Tokunaga[4] on specific NO removal for gas mixtures with water vapour content ≈2% is also demonstrated (curve 3).

The spraying of a 0.1 mol dm^{-3} KOH solution (curve 4) leads to an increase of specific NO removal at low doses (≤ 4 kGy) in spite of half the aerosol volume content. This is rather surprising because at these doses practically the only product of NO oxidation is NO_2.[4] It is unlikely that the observed effect can be connected with NO (NO_2) dissolution or by liquid-phase reactions[5] in base solution (Scheme 1).

$$NO + NO_2 + H_2O \rightarrow 2H^+ + 2NO_2^-$$

$$2NO_2 + H_2O \rightarrow 2H^+ + NO_2^- + NO_3^-$$

Scheme 1

Any appreciable contribution of these reactions (rate constants *ca.* 10^8 $dm^3\ mol^{-1}\ s^{-1}$) would need a water volume content in the irradiated gas of at least 10^{-2}. The homogeneous

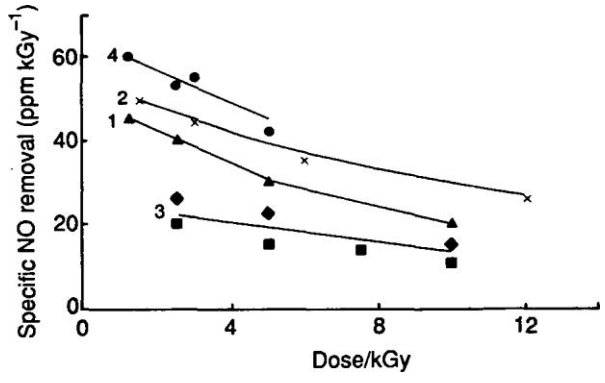

Fig. 1 Dose dependence of specific NO removal for air mixtures containing: 1, water vapour (20 mass%); 2, water aerosol (aerosol volume content 3×10^{-4}); 3, water vapour (2 mass %), ◆ our data, ■ Tokunaga[4]; 4, aerosol 0.1 mol dm^{-3} solution of KOH (aerosol volume content 1.5×10^{-4})

gas phase formation of HNO_2 and HNO_3 from NO, NO_2 and H_2O is negligible. Nevertheless, these heterogeneous reactions on the droplet surface can not be completely excluded.[6]

In this paper we attempt to explain the observed effect of NO removal at low doses by dissolution into the sprayed base solution of N_2O_3 and N_2O_4 produced in gas-phase dark reactions.

$$NO(g) + NO_2(g) \rightarrow N_2O_3(g) \quad (R1)$$

$$NO_2(g) + NO_2(g) \rightarrow N_2O_4(g) \quad (R2)$$

It must be pointed out that N_2O_3 scrubbing in the droplets may result in twice the decrease in energy consumption for NO removal, even at low doses. The characteristic times for the establishment of equilibrium in reactions R1 and R2 are too low:[7,8] $\tau_{eq} = 10^{-6}$–10^{-5} s. However, low equilibrium concentrations of N_2O_4 and N_2O_3 lead to strong demands on the characteristic times for gas-droplet transport (τ_{tr}), dissolution (τ_{aq}) and transport in droplets. The characteristic time of N_2O_4 (N_2O_3) removal (τ) may be estimated, eqn. (1),

$$\tau \sim t([N_2O_4]/[NO]_0) \quad (1)$$

where t is the time of irradiation, $[NO] \cong [NO_2] \sim [NO]_0$ is the initial admixture concentration in the gas phase, and $[N_2O_4] \sim K_{eq}[NO]_0^2$ is the gas-phase equilibrium concentration.

The stationary diffusional flux of N_2O_4 (or N_2O_3) to a droplet of radius R in proposal of its zero surface concentration is $4\pi R D_g [N_2O_4]$, where D_g is the gas-phase diffusivity (0.1–1 $cm^2\ s^{-1}$). The high removal efficiency of NO_x from the gas phase is to be expected if during the irradiation time the flux of N_2O_4 and (or) N_2O_3 affords a significant reduction in the concentration of NO and NO_2. For NO removal by N_2O_4 scrubbing we obtain eqn. (2),

$$4\pi R D_g [N_2O_4] t \approx (4/3)\pi r^3 [NO]_0 \quad (2)$$

where r is determined from $L = (R/r)^3$; L is the aerosol volume fraction. Eqn. (2) may be rewritten as eqn. (3).

$$R^2/L \approx 3K_{eq} t D_g [NO]_0 \quad (3)$$

Taking[8] $K_{eq} \cong 1$ atm^{-1} ($T \cong 330$ K), $[NO]_0 \cong 10^{-4}$ atm and $t \cong 1$ s, then $R^2/L \approx 10^{-4}$ cm^2. This estimate demonstrates that

the mechanism of gas cleaning at $L \approx 10^{-4}$ may take place only at $R \sim 1$ μm. At these values of R and L the gas-transport characteristic time $\tau_{tr} = r^2/(\pi^2 D_g) \sim 10^{-6}$ s. Similar values of τ_{tr} may also be achieved for droplets of radii ≥ 10 μm for turbulent mass transport. These conditions were realized in our experiments. Thus the processes in the gas phase are sufficiently fast.

Dissolution of N_2O_4 and N_2O_3 into droplets proceeds in reactions R3 and R4.

$$N_2O_3(g) + H_2O(l) \rightarrow N_2O_3(aq) \rightarrow 2H^+ + 2NO_2^- \quad (R3)$$

$$N_2O_4(g) + H_2O(l) \rightarrow N_2O_4(aq) \rightarrow 2H^+ + 2NO_2^- + NO_3^- \quad (R4)$$

The shift in equilibrium of reactions R3 and R4 to the right suggests a requirement to use base solutions. The necessary alkali concentration is determined from the initial NO concentration and L. There is, however, no record of the ionization rate constants of $N_2O_3(aq)$ and $N_2O_4(aq)$ in base solutions. The lifetime of $N_2O_4(aq)$ in neutral solutions[9] is in the range $\tau_{aq} = 10^{-5}$–10^{-3} s. The lifetime of $N_2O_3(aq)$ is of the order 10^{-3} s in solution at pH = 5; for N_2O_3 at pH = 10 τ_{aq} is *ca.* 10 times shorter.[10]

As regards liquid-phase molecular diffusion, the characteristic time is *ca.* 10^{-3} s (diffusion of protons in a droplet with $R \cong 10$ μm). Nevertheless, for high speed and vibrating droplets in turbulent flux the rate of mass transport may be higher.

We can see that the processes of dissolution and transport in droplets are a limiting stage and one may assume that the lower limit of the characteristic scrubbing time for N_2O_4 (N_2O_3) is of the order 10^{-4} s. According to eqn. (1) the time of NO removal for $[NO] \cong [NO_2] \sim [NO]_0 = 10^{-4}$ atm is 1–10 s, which is close to the irradiation time in our experiments. Thus, an improvement in NO removal by wet scavenging of N_2O_3 and N_2O_4 in a spraying base solution seems quite probable.

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