

REMOVAL OF NITROGEN DIOXIDE FROM INDOOR AIR BY RESIDENTIAL MATERIALS

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ABSTRACT

Nitrogen dioxide (NO_2) is a pollutant of considerable concern with respect to indoor air quality. This study has investigated the extent to which materials present in residences remove NO_2 from air. Laboratory screening experiments were carried out in two 1.64 m³ stainless steel and glass exposure chambers. Typical experiments involved exposure of materials to an initial concentration of 150 ppb NO_2 at 50% relative humidity for 12 hours. Thirty-six different materials of construction and consumer products have been examined. The results suggest that many of the residential materials are significant sinks for NO_2 . The rate of NO_2 removal is highly variable, depending on the specific material being examined. Some active materials chemically reduce NO_2 to NO , while others appear to adsorb the NO_2 . Relative humidity can influence the rate and mechanism of NO_2 removal for some materials. The laboratory results are consistent with NO_2 removal rate measurements in actual residences.

INTRODUCTION

The indoor environment contributes to total personal exposure to nitrogen dioxide (NO_2). In order to predict indoor levels of NO_2 and understand how such levels might change in response to energy conservation actions or homeowner activities, it is necessary to estimate the strength of NO_2 sources (including outside air), air infiltration rates, and indoor removal processes.

A number of studies have examined indoor sources of NO_2 , and there have been numerous studies of infiltration rate and factors affecting it. There have been fewer studies on indoor sinks for pollutants such as NO_2 . Pertinent information from some prior investigations is summarized below.

Judeikis et al. (1977) studied the reaction of NO_2 with airborne solids likely to be present in air. They report that the heterogeneous decomposition was facilitated by moisture and that the exposed surfaces eventually saturated with respect to NO_2 removal. The saturated surfaces emitted either NO or nitric acid, depending on the nature of the surface. The surfaces showed only minimal activity in terms of NO removal. Judeikis (1981) also investigated the removal of NO_2 by various building materials. The reactions were found to be capacity limited, but the surfaces were reactivated by exposure to ammonia or ammonia-containing cleaning agents. It was estimated that cement surfaces would saturate in three to six months. It was estimated that a cement-walled room could reduce the NO_2 level four- to ten-fold.

Wade et al. (1975) studied indoor/outdoor levels of NO_2 , NO , and CO around four residences with gas stoves. Special experiments in one of the homes suggested that NO_2 was removed from the indoor air with a first order rate constant of approximately 1.15 hr⁻¹, while the air exchange rate could only account for a 0.33 hr⁻¹ component of this loss. These values indicate a first order decay constant for NO_2 of 0.82 hr⁻¹ for this residence. The authors speculated that the high moisture content of the air may have enhanced the NO_2 removal mechanisms.

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Another study which obtained information on NO_2 decay in a residence was reported by Ozkaynak et al. (1982). They used a data inversion technique to derive first order decay constants in the range of $0.28\text{--}0.74\text{ hr}^{-1}$ for a single family residence in eastern Massachusetts. Using this same data set, Ryan et al. (1983) determined NO_2 decay rates from 0.35 to 1.08 hr^{-1} , with a mean of 0.66 hr^{-1} . These authors used a decay constant of 0.5 hr^{-1} for their modeling studies.

Yamanaka (1984) examined the removal rates of NO_2 , NO , and CO in a typical Japanese living room. The surfaces present consist of clay walls, wood board ceiling, floor mats, and paper slide doors. The apparent surface to volume ratio was 2.0 m^{-1} . Either a gas-fired or a kerosene-fired unvented heater was used as an emission source. For some experiments, the room was lined with polyethylene to cover the existing surface; other experiments made use of acrylic fiber carpet to cover the floor mats. Below about 55% relative humidity, the rate of NO_2 removal was about 50% greater than the infiltration rate, whether or not the room was lined with polyethylene. At higher humidities, the NO_2 removal rate varied linearly with relative humidity, and the rate was higher when the room surfaces were uncovered. The overall NO_2 removal rate at high humidity and original room surface averaged three times the air exchange rate. When the kerosene-fired heater was used, high levels of NO accompanied the emitted NO_2 . The authors concluded from the concentration patterns that NO was not oxidized to NO_2 indoors and that NO was generated by the catalytic destruction of NO_2 . Yamanaka's suggestion of NO production from NO_2 is consistent with the results of Judeikis (1981) and our residential study noted earlier, although it is far from certain that the reduction proceeds through catalysis.

Hayamizu et al. (1983) also attempted to define the reactivity of NO_2 with materials commonly found in Japanese homes. Materials included cotton, wool, two kinds of paper, and rush carpet. With the exception of the rush carpet, NO_2 removal rates by these materials were quite low. The rush carpet on the other hand removed NO_2 at a rate some 10-20 times as fast. In attempting to explain this observation, Hayamizu et al. investigated the biological denitrification occurring within the mat as a possible mechanism. They found that such could occur, but only under moist anaerobic conditions.

The efficiency for NO and NO_2 removal by several building materials and interior furnishings has been reported (Moschandreas et al. 1985). The materials were exposed to NO and NO_2 in a large chamber operated dynamically at one air exchanger per hour. Air exchange rates were determined from the decrease in CO_2 concentration. Materials included wood, plaster board, man-made and natural fabrics, carpet, linoleum, wood panel, and painted plaster. None of the materials showed much activity toward NO , but all showed some capability for reducing the NO_2 concentration. The greatest interaction with NO_2 was observed for fabrics and carpet.

Renes, et al. (1985) have reported an exposure chamber study of SO_2 and NO_2 removal in the presence of painted sheetrock, wallpaper, and carpeting. The removal rates were found to increase with increasing surface area of the material. Increases in relative humidity had a large effect on the SO_2 rate and a smaller effect on the NO_2 rate. The removal rates were generally higher for SO_2 than NO_2 , and air mixing had a significant effect on the removal rates for both gases.

Several of the reports cited above note an effect of relative humidity on NO_2 removal rate or mechanism. Macriss and Elkins (1977) have described one humidity dependent NO_2 removal process, namely absorption in condensing air conditioning systems. They found a relatively constant concentration of nitrate in the condensate from a central air conditioning system, suggesting that the rate of NO_2 removal by the system was proportional to the rate of condensation. The continuous monitoring data of Macriss and Elkins (1977) also indicate faster indoor decay of NO_2 than expected from the infiltration rate. For one set of data shown in their paper, we estimate an NO_2 reaction rate of 4.3 hr^{-1} . This NO_2 removal is attributed by the authors to the absorption process in the central air conditioning system.

The studies noted above suggest that there are materials in homes that can remove NO_2 from air at significant rates. The removal efficiency appears to increase with increasing relative humidity and to be dependent on the types of surfaces present. There is some evidence that NO_2 removal may be capacity limited for some materials and that NO can be generated during NO_2 interaction with some materials.

EXPERIMENTAL

Laboratory screening experiments to investigate NO_2 removal by residential materials were conducted using two 1.64 m^3 stainless-steel chambers. The chamber apparatus is shown schematically in Figure 1. The chambers are constructed of stainless steel, with a glass window front and back. Each chamber has a surface area of 7.5 m^2 , and a surface to volume ratio of 4.6 m^{-1} . The chambers are outfitted with large front doors in front, and stainless steel racks inside. A mixing fan is located at the inside top of each chamber.

The chambers are supplied with high purity air from a commercial clean air generator. A large reservoir between the chambers serves to store clean air under pressure for high use periods. The chambers are fitted with pressure gauges, pressure relief valves, vented exhaust tubes, syringe injection ports, and air sampling ports. Solenoid valves are used to control all air handling operations, including sampling, purging, and addition of dilution air. The valves are controlled by a microcomputer. Regulated flow of clean air into the chambers is controlled by mass flow controllers. The chambers are humidified by passing a measured portion of the purified air through a baffled hot water humidifier.

The monitoring instruments used in the exposure chamber experiments are noted in Table 1. All instruments are continuous monitors. The instruments are calibrated using a commercial dynamic dilution/gas phase titration system, with the source mixtures referenced to National Bureau of Standards primary standards.

The signals from all the instruments in Table 1 are monitored by the computer, which serves as a data acquisition and data reduction system. The instruments are time-shared by the two chambers.

Characterization experiments show that the chamber dilution rates are very reproducible at 0.018 hr^{-1} . Duplicate experiments with selected residential materials demonstrate that the NO_2 behavior in the two chambers is nearly identical.

In preparation for an experiment, each chamber is loaded with approximately 3.3 m^2 (gross surface area) of exposed surface of the residential material under study. This surface area in the 1.64 m^3 chamber simulates the surface-to-volume ratio ($\sim 2 \text{ m}^{-1}$) of an empty room in a residence. After loading, the chambers are purged with pure air and brought up to 50% relative humidity. An inert gas, sulfur hexafluoride (SF_6), is used to monitor the dilution of the chamber as pure air is added to the chambers to compensate for air removed during sampling. After humidification, the dilution tracer is injected into each chamber. Finally, NO_2 is injected into the chambers with the mixing fans on. The NO_2 is injected by syringe from a cylinder of 1000 ppm NO_2 in air. After the chamber air is mixed, the fans are turned off for the remainder of the experiment. Decay of NO_2 and production of NO are monitored for 12 hours. The temperature, relative humidity, and dilution rate are monitored throughout the experiment.

RESULTS AND DISCUSSION

It seems clear from previous studies that NO_2 is being removed from indoor air by processes other than just air exchange. This study was designed to investigate whether surfaces present in residences may be active in removing NO_2 from the air and to determine the relative importance of different residential materials as NO_2 sinks.

The first phase of this study has involved screening a number of materials of construction and consumer products to determine their reactivity with respect to NO_2 removal. Each screening experiment was carried out over a 12-hour reaction period. All experiments were initiated with 150 ppb NO_2 at 50% relative humidity.

A plot of the data from a representative experiment with fiberglass furnace filters is shown in Figure 2. The plot shows the natural logarithm of the concentrations of SF_6 , NO_2 , and NO versus time. The slope of the NO_2 curve is used to calculate a total NO_2 removal rate constant in units of hr^{-1} .

The total NO_2 removal rate is made up of three components:

- dilution
- removal by chamber surfaces
- removal by the test material

To determine the rate due to the test materials, the rates due to dilution and chamber surface are subtracted from the total removal rate. Dilution is determined from the slope of the SF₆ curve. Loss of NO₂ to the chamber surfaces is determined from blank experiments in which the chambers are operated in the absence of any test materials.

The data in Figure 2 illustrate another important point. In this particular experiment, a significant fraction of the NO₂ removed from the air is recovered as NO. This suggests that a chemical reduction is occurring. Some component of the furnace filter is reducing NO₂ to NO, either by chemical reaction or by catalysis. Conversion of NO₂ to NO is very beneficial in terms of potential effects on occupant health. There is no ambient air standard for NO, but the ACGIH time weighted average is 25 ppm, which is considerably higher than the 0.05 ppm annual average NO₂ standard. Thus, conversion of NO₂ to NO represents a net improvement in air quality in terms of potential health effects.

As noted above, there was significant conversion of NO₂ to NO in the experiment with furnace filters (Figure 2). Reduction to NO has been observed in many of the residential materials screening experiments. On the other hand, many of the materials remove NO₂ rapidly without producing any NO. These observations indicate that there are at least two mechanisms leading to NO₂ removal: reduction to NO and physical removal from the air. The nature of the latter removal process is unclear, but it may consist of adsorption followed by chemical reaction at the surface. Future experiments are planned to investigate this phenomenon.

Screening experiments have been conducted with 36 residential materials. Each material has been exposed to 150 ppb NO₂ at 50% relative humidity, and the rate of NO₂ removal from the chamber air was measured. The materials employed in these experiments and the respective NO₂ removal rates are listed in Table 2. All the data in Table 2 have been corrected for NO₂ removal by dilution and reaction with the chamber surface. It is important to note that the removal rates shown in the table pertain to the conditions of these experiments, and that different surface to volume ratios would likely give different results.

In order to put the laboratory results in perspective, we have used the laboratory data to calculate an NO₂ removal rate in a typical residence for comparison with rates that were measured experimentally. Use of the laboratory data for this purpose should be done with caution in view of the different surface to volume ratios and mixing rates involved. However, such a comparison may reveal useful information regarding the NO₂ removal process. The calculated rate makes use of the information in Table 2, along with estimates of the surface area of the major residential surfaces and the volume of the residence. The laboratory results suggest an NO₂ removal rate of about 1.2 hr⁻¹ in our example residence, whereas measurements made in this residence yield removal rates ranging from 0.7 to 1.7 hr⁻¹. The calculated removal rate should be viewed as a first approximation only, in view of the uncertainties in estimating surface areas and volumes for a typical residence and transferring the results of laboratory experiments at one surface to volume ratio to a very different S/V in a residence. The comparison does suggest however, that the laboratory results are consistent with NO₂ removal rate measurements in actual residences.

CONCLUSIONS

A study of NO₂ interaction with residential materials has been carried out using two 1.64 m³ laboratory exposure chambers. The study has shown that numerous residential materials remove NO₂ from air and that the rate of removal varies widely among the materials. As an example, under the conditions of our experiments, window glass removed essentially no NO₂ during a 12-hour exposure, while cement block removed all of the NO₂ within 30 minutes. We have found from a review of the literature and experiments in actual residences, that the NO₂ removal rate in homes, after correction for infiltration of outside air, is often in the range of 0.5 to 1.5 hr⁻¹. Our laboratory results suggest an NO₂ removal rate of 1.2 hr⁻¹ for a typical residence, which agrees reasonably well with measurements made in this and other residences.

Two mechanisms of NO₂ removal have been observed during the laboratory experiments. For some materials, NO₂ is reduced to NO, while for many of the materials, NO₂ is removed completely from the system. In at least one case, the mechanism has been observed to shift from removal to reduction with increasing relative humidity. Other factors that may affect the removal process include NO₂ concentration, temperature, and possibly other external variables such as the concentration of other indoor pollutants.

The results of this study, while still preliminary, provide useful information on the relative importance of residential materials as NO₂ sinks. These results also suggest the

possibility of mitigating the effects of indoor NO_2 by reducing the NO_2 concentration through judicious selection of construction materials/furnishings. More detailed studies of the removal rates, and especially the removal mechanisms, are continuing.

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ACKNOWLEDGMENT

This research was supported by the Gas Research Institute.

TABLE 1
Instrumentation for Chamber Experiments

Variable	Technique
NO/NO_x	Chemiluminescence
Inert Tracer (SF_6)	Flame Photometry
Temperature Dew Point Temperature Relative Humidity	Thermocouple Controlled Condensation Derived from T and DPT

TABLE 2
Results of NO₂ Exposure Screening Studies

Material	NO ₂ Removal Rate, hr ^{-1a}
Masonite	4.1
Ceiling Tile	1.9
Plastic Storm Windows	0
Galvanized Metal Duct	0
Furnace Filters (New)	1.4
Furnace Filters (Used)	0.64
Formica Counter Top	0
Particle Board (Pressed Wood)	0.74
Vinyl Tile	0
Asphalt Tile	0
Plywood (1/4 in.)	2.5
Plasterboard	>8.3
Vinyl-Coated Wallpaper	0.86
Walltex Covering	0.11
All Vinyl Wallcovering (Paper Backing)	1.9
Polyethylene Sheet (1/4 mil)	0
Cotton/Polyester Bedspread	2.7
Cement Block	8.4
Ceramic Tile	0.69
Asphalt Tiles (Waxed)	0.12
Window Glass	0.06
Polyurethane Foam (1/4 in.)	3.7
NH ₃ -Cleaned Window Glass	0.01
Bricks (Used)	4.2
Plasterboard (Painted)	2.6
Furnace Heat Exchanger (Used)	0.05
Polyester Carpet (Sculptured)	1.9
Wool Carpet	6.0
Acrylic Fiber Carpet	2.0
Nylon Carpet	2.0
Acrylic Carpet	1.5
Dehumidifier	1.25
Oak Paneling	1.0
Cotton Terry cloth	0.3
Wool (80%)/Polyester (20%) Fabric	0.3

^aFirst order removal rate constant in hr⁻¹; multiply by 100 for percent hr⁻¹.

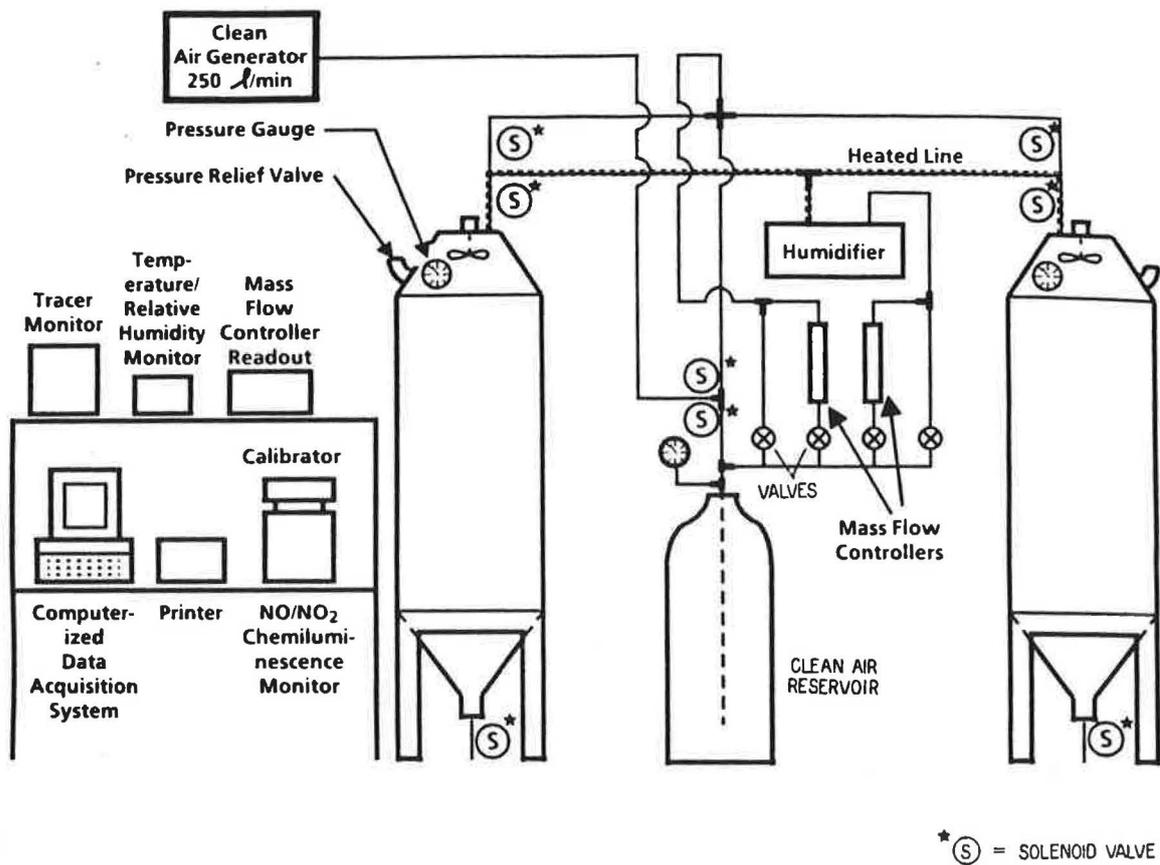


Figure 1. Schematic diagram of exposure chambers used to examine NO₂ removal by residential materials

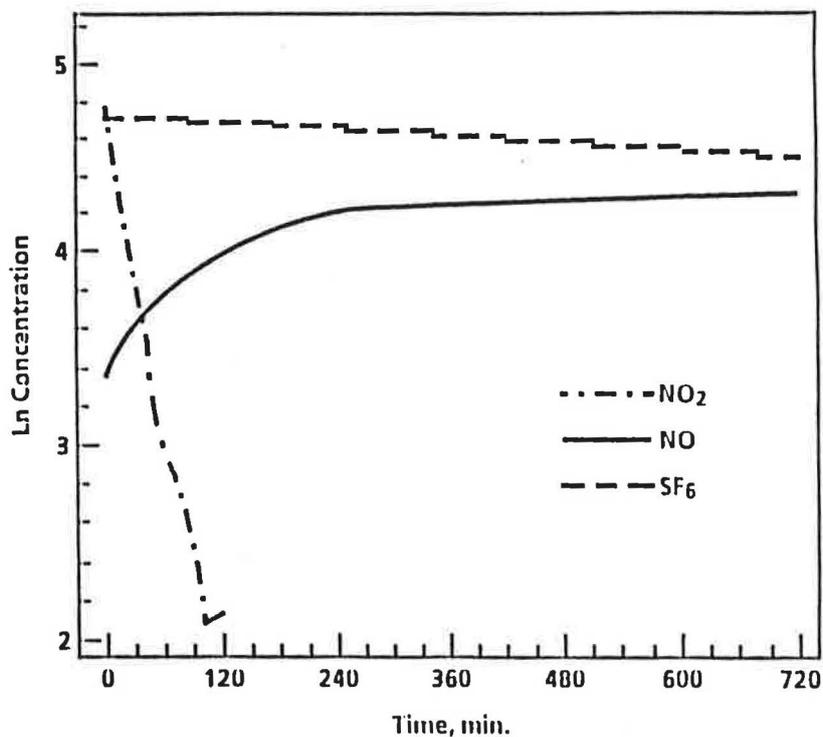


Figure 2. Natural log plot of NO₂, NO, and SF₆, vs. time for exposure of new furnace filters to 150 ppb NO₂ at 50% relative humidity