Indoor Nitrogen Oxides Occurrence, Modeling and Prediction

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Abstract: Outdoor air quality, building materials, HVAC (Heating, Ventilation, Air Conditioning) systems and people activity are important factors in human exposition of polluted indoor air. The degree of signification varies in dependence on pollution character and its sources. Buildings eliminate significantly people exposition of outdoor pollutants, but on the other hand, buildings are significant source of indoor pollution. The contamination of indoor air is largely from the use of gas for heating and cooking appliances. A comprehensive analysis of indoor air pollution by nitrogen oxides shows that the extent of indoor air pollution and consequent exposure varies as a result of many factors mainly the differing distribution of appliances and their level of use. This study aims to formulate a mathematical model for the production of nitrogen oxides indoors. The physical processes that determine the concentrations of indoor nitrogen oxides as a function of outdoor concentrations, indoor emission rates and building characteristics have been mathematically described. The mathematical model developed has been parameterized for typical Slovak residences. The modeling of the occurrence of indoor nitrogen oxides and verification of the model is presented in this paper.

Key words: Indoors, nitrogen oxides, occurrence, prediction, modeling, verification.

1. Introduction

NO (Nitrogen monoxide) and NO₂ (nitrogen dioxide) are gases produced by high temperature combustion through reactions between nitrogen and oxygen. Both nitrogen in the fuel and nitrogen in the air can participate in the reactions. Formation of NO can be followed by further oxidation into NO₂ in the atmosphere. NO₂ is the most toxic of the nitrogen oxides (grouped generically as NO_x) and it is very important from the health point of view. During several last years the emissions of nitrogen oxides have increased. The mean daily outdoor nitrogen oxides concentrations achieve value 107.1 µg·m⁻³ in the winter and 35.2 µg·m⁻³ in the summer. The mean daily indoor nitrogen oxides concentrations achieve value 125.3 µg·m⁻³ in the winter and 48.5 µg·m⁻³ in the summer [1]. The most important indoor source of nitrogen oxides is gas burning in the kitchen. Finally concerning to indoor

environment, indoor air can be contaminated by using gas for heating and cooking and this probably involves a certain health hazard. Practical experiences show, that range of indoor nitrogen oxides concentration depends on energy conservation tendency interpret with ventilate level decrease [2]. The highest nitrogen oxides concentrations are achieved during gas burning in the kitchen in dependence on intensity of gas burning, amount of gas burned and on room disposition [3]. In the present work indoor NO_x concentrations were measured in order to understand their contribution to indoor sources and so to human exposure.

2. Indoor and Outdoor NO_x Occurrence during the Year

Indoor sciences have been studied over the last twenty years at Technical University of Košice in Slovakia. Initially the monitoring of indoor pollutants (radon, particles, VOCs, odours, nitrogen oxides, etc.) was undertaken in buildings located in the east part of Slovakia. Seasonal differences in pollutant levels were

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confirmed. It was shown that for this study which looked at indoor NO_x concentrations were significantly higher than outdoor ones especially in the winter period (Fig. 1). All buildings studied used gas appliances, mainly in the kitchens [4].

3. Method of NO_x Concentration Measurement

Measurements were made to detail NO_x production and determine the resultant indoor concentrations while gas appliances were being used. The intensity of gas combustion varied in the range $0.1 \text{ m}^3 \cdot \text{h}^{-1}$ – $0.7 \text{ m}^3 \cdot \text{h}^{-1}$. As kitchens had been identified as the most polluted rooms measurements were taken in the kitchens. The levels of background concentrations of NO , NO_2 and NO_x were monitored. The increase and decrease of NO_x concentrations was found at the same time.

The investigation included online gas measurement for NO , NO_2 and NO_x by the “Thermo Environmental Instruments Inc. — model 42 — Chemiluminiscence NO – NO_2 – NO_x Analyzer”. This analyzer was located in the middle of the room, at the level of the breathing zone of a sitting person — 105 cm above the floor. The results showed concentration peaks during the cooking, but with large differences from using different intensities of gas burning.

4. Results

The concentrations of NO_x after 1 h gas combustion were shown to depend on the level of gas consumption ranging from $0.1 \text{ m}^3 \cdot \text{h}^{-1}$ to $0.7 \text{ m}^3 \cdot \text{h}^{-1}$ (Fig. 2).

The changes in NO_x concentration over the intensity range of gas consumption ($0.1 \text{ m}^3 \cdot \text{h}^{-1}$ to $0.7 \text{ m}^3 \cdot \text{h}^{-1}$) were studied. The changes while allowing the combustion process to continue at maximum for 60 min, and for decreasing rates of gas usage, were then followed over the next 90 min after combustion had stopped. The pattern of oxides formation at a gas usage rate of $0.1 \text{ m}^3 \cdot \text{h}^{-1}$ is given in Fig. 3. It is evident that an essentially linear increase of NO , NO_2 and NO_x concentrations occurred during the whole combustion

Fig. 1 Mean indoor and outdoor NO_x concentrations throughout a year.

Fig. 2 The NO_x concentrations for gas consumption range studied.

Fig. 3 The concentrations of nitrogen oxides at gas usage rate of $0.1 \text{ m}^3 \cdot \text{h}^{-1}$.

period to a final maximum value after 1 h when gas usage was stopped (NO 1,357.4 $\mu\text{g}\cdot\text{m}^{-3}$, NO_2 428.5 $\mu\text{g}\cdot\text{m}^{-3}$ and NO_x 1,785.9 $\mu\text{g}\cdot\text{m}^{-3}$). Decrease in concentration was then followed for a period of 90 min, after which period the concentrations were NO 209.8 $\mu\text{g}\cdot\text{m}^{-3}$, NO_2 69.4 $\mu\text{g}\cdot\text{m}^{-3}$ and NO_x 279.1 $\mu\text{g}\cdot\text{m}^{-3}$.

Importantly, it should be noticed that the concentration of NO_2 after 1 h of gas combustion (428.5 $\mu\text{g}\cdot\text{m}^{-3}$) more than exceeded double the limit value according to the Slovak standard (200 $\mu\text{g}\cdot\text{m}^{-3}$). The limit was exceeded after 10 min from the start of combustion (270.9 $\mu\text{g}\cdot\text{m}^{-3}$) and concentrations remained above the limit for the next 100 min (228.6 $\mu\text{g}\cdot\text{m}^{-3}$) [5].

5. Mathematical Modeling

Designing and modeling can substantially contribute to problem solution and to obtaining new understanding concerning system behavior with respect to air component dynamic changes. A mathematical description of the processes can generalize the experimental results and so they may be used to interpret other processes physically similar to those introduced in the model.

Although modeling doesn't achieve all the rules of similarity, it does provide overall information concerning systems' behavior, which is only a little different from a real situation. Also, although it is an approximation the model does simplify description of the real physical measurements.

5.1 Prediction of NO_x Occurrence

The difficulty of predicting NO_x emissions during combustion of fossil fuels is caused mostly by the complexity of the mechanisms of formation of the NO_x , which depend on many factors. Some partial mechanisms have not been completely clarified so far and so it is not possible to describe them exactly. In consequence, empirical correlations between the fuel properties, combustion regime and NO_x emissions cannot be properly calculated. This affects the degree

to which calculations can be informative in a mathematical model of indoor NO_x production. The final result has to be assembled from the results obtained from statistically suitable collections of measurements as well as more controlled laboratory measurements [5].

5.2 Input Parameters

The research task to describe NO_x production in combustion process relies on the measure of NO_x influenced by such parameters which directly characterize the combustion process, i.e., intensity of gas combustion I ($\text{m}^3\cdot\text{s}^{-1}$), exposure period t (s), amount of indoor air m (kg) and air change n (s^{-1}).

All the given variables are defined using basic dimensions, allowing their direct use for dimensional analysis to create the mathematical model of NO_x production. All the variables can be simply measured directly during combustion allowing us subsequently to compare the NO_x production under particular working conditions on the chosen combustion device on the basis of direct measurements and by means of the created mathematical model described in the following section [6].

5.3 Dimensional Analysis Application

The mathematical model describing NO_x formation is based on the formation of dimensionless arguments, π_i , from the stated variables that influence formation of the oxides of nitrogen. The valuable property of these arguments is that in all existing systems of units they have the same numerical size and they have no dimension.

Formation of a mathematical model rests on derivation of functional dependence from the expressed dimensionless variables, which in general always has exponential character. Transformation of this function into logarithmic co-ordinates corresponds to a linear character that makes the work with the model easier and enables one to determine simply the parameters of linear function.

The model given here has universal validity for all combustion devices that have at least approximately similar geometric characteristics. For every combustion device the parameters of linear function, i.e., regression coefficients, have to be determined separately.

The mathematical formula of nitrogen oxides production by application the dimensional analysis is [4]:

$$NO_{xi} = 10^9 \cdot A \cdot t^{B-} \cdot n^B \cdot m \cdot I^{-1} \quad (1)$$

where, A and B are regression coefficients calculated by the method of least squares.

$$NO_x = NO_{xo} + NO_{xi} \quad (2)$$

where,

NO_{xi} —indoor nitrogen oxides concentration;

NO_{xo} —outdoor nitrogen oxides concentration.

Eq. (2) presents a mathematical model of NO_x production through using gas appliances in the kitchen [4].

6. Verification of Mathematical Model

The mathematical model was verified for various amounts of gas consumption in the range of 0.1 – $0.7 \text{ m}^3 \cdot \text{h}^{-1}$. As illustration verification for gas consumption of $0.1 \text{ m}^3 \cdot \text{h}^{-1}$ using a model experimental room is given below. The amount of air was 28.28 kg and the air change rate $3.56 \times 10^{-4} \text{ s}^{-1}$. The air change rate was determined on the basis of decreasing NO_x concentration per hour.

On the basis of measured input parameters, NO_x concentrations were determined through the located constants and regression coefficients obtained by the method of least squares. These values are presented in the Table 1.

The relationship for NO_{xi} production at a gas consumption rate of $0.1 \text{ m}^3 \cdot \text{h}^{-1}$ is obtained from:

$$NO_{xi} = \frac{4.0E-09 \cdot t^{1.8420-1} \cdot n^{1.8420} \cdot m}{I} \quad (3)$$

The values of measured and calculated NO_x concentrations are compared in Table 2. The differences

Table 1 Regression coefficient values.

Gas consumption	A ($\text{m}^3 \cdot \text{h}^{-1}$)	B ($\text{m}^3 \cdot \text{h}^{-1}$)
0.1	4.0000E-09	1.8420
0.2	2.0000E-08	1.7765
0.3	2.0000E-07	1.8179
0.4	3.0000E-07	1.8593
0.5	4.0000E-07	1.6603

Table 2 The measured and calculated NO_x concentrations.

T (min)	$NO_{x\text{meas.mean}}$ ($\mu\text{g} \cdot \text{m}^{-3}$)	$NO_{x\text{calc}}$ ($\mu\text{g} \cdot \text{m}^{-3}$)	Deviation (%)
5	204.7	243.9	20.67
10	489.5	420.6	16.34
15	671.5	583.2	16.97
20	854.5	737.3	19.54
25	1,013.0	885.4	18.43
30	1,131.8	1,028.9	17.10
35	1,320.8	1,168.6	13.89
40	1,477.9	1,305.1	12.15
45	1,565.1	1,439.0	10.77
50	1,660.9	1,570.5	10.02
55	1,711.7	1,700.0	11.53
60	1,785.9	1,827.7	11.25

between measured and calculated NO_x concentrations are considered acceptable. They can be explained, in that the selection of relevant parameters is a simplification, their degree of involvement and how many of all the factors on which NO_x production depends they represent is unknown.

7. Conclusions

The study of indoor pollutants affecting indoor air quality is a modern problem. One solution is the use of mathematical methods to predict the level of pollutant concentrations. This paper proposes a possible mathematical approach to modeling the occurrence of NO_x indoors. Correct selection and clear determination of all relevant parameters at the beginning of construction of the mathematical model are important. Through comparison with experimental measurements we have confirmed that NO_x production is mainly affected by intensity of gas combustion, exposure period, and rate of air change. A mathematical description of the physical processes influencing NO_x

production has been derived and used to predict occurrence of these gases.

The model was verified with satisfactory results for gas consumption in the range $0.1\text{--}0.7\text{ m}^3\cdot\text{h}^{-1}$. Differences between measured and calculated indoor NO_x concentrations are probably because the selected relevant variables for construction of the mathematical model do not give a complete and exactly true picture of the combustion processes leading to NO_x production. Results from the mathematical modeling approach can be improved thorough better understanding of precise input parameters which will make the process applicable to building design and building management.

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