

A Near Field-Far Field model for assessing Oxygen Deficiency Hazard

Elena Stefana^a, Filippo Marciano^{a,*}, Paola Cocca^a, Marco Alberti^a

^aDepartment of Mechanical and Industrial Engineering, University of Brescia, via Branze 38, 25123 Brescia, Italy

* Corresponding author. Tel.: +39 0303715834; fax: +39 0303715722

E-mail addresses: elena.stefana@ing.unibs.it (E. Stefana), filippo.marciano@unibs.it (F. Marciano), paola.cocca@unibs.it (P. Cocca), marco.alberti@unibs.it (M. Alberti)

Abstract

Oxygen Deficiency Hazard (ODH) due to inert gas releases can be assessed by the use of predictive models. Several models are available in the literature: the majority of them can be classified as “well-mixed” models because they assume the existence of completely and instantaneously well mixed air. In order to provide a more precise estimation of the indoor oxygen level in the breathable air close to a release point, we propose a Near Field-Far Field (NF-FF) model in which the Near Field volume is an output and can vary over time. The trend of the Near Field size can be a useful data for the risk assessor in order to determine the safety distance from point source releases, and improve the emergency response plan. Starting from balances of mass of air and moles of oxygen both in the Near Field and in the Far Field, the objective of our model is to predict the volume of the Near Field that contains a limit value for the oxygen concentration at every time instant. The approach includes several analytical formulas that model the different flows occurring in each field and between the two fields. In particular, we assume the existence of inert gas releases, forced and natural ventilation airflows, interzonal airflows, and air that has to move from the Far Field to the Near Field, or vice versa, for assuring a limit value for the oxygen concentration in the Near Field. Finally, examples of the application of this model in some case studies available in the literature are presented and discussed.

Keywords

ODH; Two-zone; Asphyxiation risk; Mathematical model; Inert gas; Occupational health

Nomenclature

%_{we,f} = percentage of the free volume of the working environment (%)

\dot{Q} = volumetric flow rate ($\text{m}^3 \text{s}^{-1}$)

$\dot{\beta}$ = interzonal volumetric airflow rate between the NF and FF ($\text{m}^3 \text{s}^{-1}$)

b = binary variable (dimensionless)

C = concentration by volume (%)

FSA = free surface area of the NF (m^2)

I = number of inert gases (dimensionless)

IMP = number of impurities (dimensionless)

J = number of failure modes (dimensionless)

k = binary variable (dimensionless)

m = mass (kg)

n = mole (mol)

p = pressure (Pa)

P = probability (dimensionless)

pp = partial pressure (Pa)

r = distance of the worker from the release point; in the case of hemisphere-shaped NF, it is the radius of the hemisphere (m)

R = ideal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$)

Rel = reliability (dimensionless)

S = number of ventilation systems (supply air or return air sub-systems), or storage and/or distribution systems (dimensionless)

s = random airspeed at the boundary of the NF (m s^{-1})

T = temperature (K)

t = time (s)

V = volume (m^3)

Y = number of other pure inert gases included in the inert gas (excluding the main pure inert gas), or in the air introduced in or drawn from the working environment (dimensionless)

β = interzonal volume between the NF and FF (m^3)

δt = time instant or infinitesimal time (s)

ϕ = volume fraction (%)

Subscripts

a = accidental release

air = air

atm = atmospheric value

f = free

FF = Far Field

i = i-th inert gas

ig = inert gas released into the working environment

imp = impurity

in = air introduced into the working environment by supply air sub-systems of ventilation systems

j = j-th failure mode

mec = air drawn from the working environment by return air sub-systems of ventilation systems in a mechanical (forced) way

nat = air introduced into or drawn from the working environment in a natural way

NF = Near Field

O₂ = oxygen

occ = occupied

oe = outdoor environment

out = air drawn from the working environment by return air sub-systems of ventilation systems

s = s-th system (supply air sub-system of ventilation systems, return air sub-system of ventilation systems, or storage and/or distribution system)

v = voluntary release

we = working environment

x = x-th main pure inert gas included in the inert gas

y = y-th other pure inert gases included in the inert gas (excluding the main pure inert gas), or in the air introduced into or drawn from the working environment

1 Introduction

Oxygen Deficiency Hazard (ODH) occurs when the indoor oxygen content drops to a level that may expose workers to the risk of asphyxiation. Details about the risk assessment of ODH can be found in Stefana et al. (2015; 2016).

A relevant cause of ODH is represented by inert gas releases. Inert gases are simple asphyxiant substances that dilute the available atmospheric oxygen. These substances are usually present in process industries and used for purging and identifying leaks in plants or pipework, for creating inert atmospheres inside or outside equipment, and for preventing unintentional chemical reactions. Furthermore, they are exploited for replacing air in all operations in which the presence of oxygen is dangerous or damaging: “replacement of oxygen with nitrogen can eliminate a dust explosion hazard while at the same time introducing an asphyxiation hazard” (Amyotte, 2014). Details about the use of inert gases and the reduction of oxygen for preventing explosions are also reported in Amyotte (2013).

ODH can be estimated thanks to the use of predictive models able to determine the oxygen level in a working environment. In some working environments, airflow mixing is created and thus a well-mixed model can predict quite well the oxygen content. In other cases, air in a workplace is not well-mixed and is subject to stratification phenomena. In these cases, a well-mixed model for estimating the indoor oxygen level can underestimate the content of this gas in working environments, potentially causing errors in the assessment of ODH.

This consideration is valid in general: for example, Sakhvidi et al. (2013) underline that a well-mixed room model “underestimates the concentration in the locations near the pollution sources”, and Danyluk and Hon (2006) highlight that “in real situations, the air does not tend to be perfectly mixed in rooms and, even with various corrective factors, these models tend to underestimate exposures close to the source”.

In order to reduce some of these errors, safety managers can adopt a Near Field-Far Field (NF-FF) model, which better estimates the gas content near the release point, where the gas level is supposed to be lower than the average gas level in the room. In particular, this kind of approach allows to take into account, even though partially, the deviations from the completely mixed assumption. NF-FF (or two box) model considers the spatial variability in exposure intensity and imperfect air mixing (Keil, 2000; Keil et al., 2009; Persoons et al., 2011; Ramachandran,

2005; Spencer and Plisko, 2007). In accordance with Jayjock et al. (2011b), the NF-FF approach, as it currently exists, is a first attempt to address the fault of the well-mixed model.

The NF-FF model was originally described by Hemeon in 1963 (Hemeon, 1963), and then developed by Nicas in 1996 (Nicas, 1996). In particular, Nicas (1996) provides the derivation of the dynamic concentration equations. The NF-FF model is a modified well-mixed model (Jayjock et al. 2011a; Sakhvidi et al., 2013), which attempts to capture the effect of source proximity on exposure and thus the exposure of workers close to the contaminant source (Ramachandran, 2005). This model has the objective to predict the Near Field (NF) and Far Field (FF) exposure concentrations (Vadali et al., 2009). Note that these two fields are a subdivision of the working environment, and the sum of their volumes is the overall volume of the working environment.

In the literature there are several examples of application of this model to estimate the concentration of different chemicals: isoflurane (Sakhvidi et al., 2013), benzene (Nicas et al., 2006), solvent (Spencer and Plisko, 2007), methanol vapours (Gaffney et al., 2008), dusts (Jones et al., 2011), sulfur hexafluoride (Furtaw Jr. et al., 1996), laser-generated particulate matter (Lopez et al., 2015), cleaning products (Earnest and Corsi, 2013), toluene (Hofstetter et al., 2013), and unspecified substance (Feigley et al., 2002). One of these studies (Nicas et al., 2006) predicts concentrations using a non-constant emission rate, as done also in other papers: for example, Nicas and Armstrong (2003b) (a spreadsheet to compute a sine function emission rate), Nicas and Neuhaus (2008) (a formulation valid in the case of a variable emission rate), Nicas and Armstrong (2003a) (Excel spreadsheets and a Matlab code for studying the two-zone model with a constant emission rate and an exponentially decreasing contaminant emission rate), and Nicas (2016) (a revisited study of Nicas and Neuhaus (2008) with constant application of chemical mass and exponentially decreasing emission of the mass applied).

Although the NF-FF approach could allow a more precise prediction of oxygen level with respect to the well-mixed approach, none NF-FF model for ODH assessment is available in the literature. Therefore, the aim of this paper is to develop a new model for estimating the volume that contains a limit value for the oxygen concentration (settable by the risk assessor) based on a NF-FF approach.

2 Literature review

Seventeen models usable to estimate the indoor oxygen level in a working environment, using different parameters and considering several aspects, are published in scientific journals or appear in technical documents. These models are listed in the following in alphabetical order by authors: (1) Adamowski (2010); (2) Alicino et al. (2008); (3) Arenius et al. (2002); (4) Augustynowicz (1993); (5) Blyukher (1995); (6) Chorowski et al. (2006); (7) Crozier (2008); (8) Delayen et al. (2001); (9) Fermilab (2015); (10) Iarocci (1994); (11) Jefferson Lab (2014); (12) Jia and Wang (2002); (13) Luke (2004); (14) Miller and Mazur (1984); (15) Morgan (2014); (16) SLAC (2015); and (17) Stefana et al. (2016).

Stefana et al. (2015) perform a systematic review of the available literature about predictive models estimating the indoor oxygen level in working environments where there can be inert gas releases. This systematic review analyses the first sixteen models listed above, concluding that none of them satisfies the following indicators:

- possibility to set initial indoor air composition;
- possibility to set indoor temperature in time;
- possibility to set initial total pressure of indoor air;
- possibility to set total pressure of indoor air in space and/or in time;
- possibility to consider working environment, and plant layout or plant logic diagram;
- possibility to set outdoor oxygen concentration in space and/or in time;
- possibility to set outdoor air composition in space and/or in time;
- possibility to set natural ventilation and infiltration airflow rate in time;
- possibility to consider reliability of Heating, Ventilation, Air Conditioning, and Refrigeration (HVAC-R) systems and/or plant components;
- presence of examples of reliability values of plant components;
- possibility to consider more failures simultaneously;
- possibility to evaluate releases of more substances and/or mixtures simultaneously;
- possibility to model substances and mixtures like real gases;
- possibility to set composition of release mixtures in time;
- possibility to consider release flow rate in space;
- possibility to set pressure of release flow rate in space.

The seventeenth model by Stefana et al. (2016) seeks to overcome some of these weaknesses, such as the possibility to set initial indoor air composition, consider reliability of HVAC-R systems, and evaluate releases of more substances and/or mixtures simultaneously. However, this last model does not have the possibility to estimate indoor oxygen level in space.

In addition to these aspects, the majority of the seventeen models can be classified as well-mixed models: the air in the working environment is completely and instantaneously well mixed, and the outputs are the same at any point in the workplace. Well-mixed models can be useful in working environments where sources of a contaminant are

spread in the overall volume, or where there are conditions that could mix the air in the room (Keil, 2015). In addition, this type of models can give a reasonable estimate of exposure intensity in situations where there are dispersed evaporation sources (Keil and Murphy, 2006), or when workers are not very close to the source (Keil et al., 2009; Ramachandran, 2005). None of the seventeen models in the literature adopt a NF-FF approach in order to estimate the indoor oxygen level in space. The new model proposed in this paper aims to overcome this weakness.

3 Mathematical model

3.1 Objectives of the model

The main objective of this model is to estimate in time the volume of the NF that contains a limit value for the oxygen concentration defined by the risk assessor. In particular, we are interested in understanding which NF volume allows to prevent the asphyxiation risk (i.e. due to the fact that the operator is exposed to an oxygen concentration lower than the safe one) or, in other words, how the NF size varies over time, changing the boundary area where there can be an oxygen deficient atmosphere. Indeed, asphyxiation risk appears particularly high in the proximity of the release zone. This model is applicable regardless of the country, the company, and the type and size of working environment.

The working environment is constituted by a NF and a FF; the sum of their volumes is equal to the overall working environment volume. The NF can have different shapes and the risk assessor can choose the most appropriate one to the working environment. The model is developed considering that the NF is always completely contained in the working environment volume, irrespective to the NF shape.

The model is based on the balances of mass of air and moles of oxygen, both in the NF and in the FF. In particular, in the NF there are the sources of inert gases, and thus the oxygen content can be potentially less than the one in the FF because of the proximity to the releases of inert gases. Inert gases can be released voluntarily and/or accidentally. Voluntary releases depend on the reliability of the storage and/or distribution systems, while accidental releases on the probability that a storage and/or distribution system fails and a specific failure mode occurs. In the model, releases can be instantaneous, finite/temporary, or continuous, of pure gas or mixtures (also containing some impurities).

For safety reasons and similarly to other NF-FF models (e.g. Keil et al., 2009), we consider that the supply air sub-systems of ventilation systems, the return air sub-systems of ventilation systems, and the natural ventilation are in the FF. Both supply air and return air are provided by HVAC-R systems, which are characterised by reliability parameters, airflow rates, and compositions. In particular, the composition of the air supplied by each sub-system is settable in time by the safety manager, while the composition of the air drawn from each sub-system is equal to the indoor composition in the previous instant.

As reported in other NF-FF models (e.g. Nicas, 1996; Keil et al., 2009), this type of model involves interzonal exchanges between the two fields. Therefore, we assume the existence of an interzonal airflow that is a limited exchange of air that depends on the free surface area of the NF in the time instant previous to the one considered, and the random airspeed at the boundary of the near field. This interzonal airflow occurs in both directions: from the FF to the NF (with the air composition of the FF), and from the NF to the FF (with the air composition of the NF). From the point of view of the oxygen content, this flow provides a positive contribution to the oxygen level in the NF. This consideration derives from the following assumptions: (1) the inert gas releases occur only in the NF, (2) there are no releases of mixtures with high oxygen content, and (3) the supply air sub-systems of ventilation systems, the return air sub-systems of ventilation systems, and the natural ventilation are only in the FF.

Note that there is an interzonal airflow at a particular instant if in the previous instant there was a NF. Indeed, for the assumptions and the mathematical formulation of our model, not in all instants there could be a NF or a FF. There is a NF if there is a release such as to create a volume with an oxygen concentration equal to a fixed limit value for the oxygen concentration. There is not a NF (and, therefore, there is only a FF) if in all points of the working environment the oxygen concentration is greater than the fixed oxygen concentration limit. On the contrary, there is not a FF (and, thus, the working environment is all NF) if in all points of the working environment the oxygen concentration is equal to the fixed limit value for the oxygen concentration. In this case, the iterations of the model end because the NF volume is equal to the working environment volume.

As a consequence, oxygen concentrations below the fixed limit value for the oxygen concentration are not permitted by the model.

In Appendix 1 we report a complete list of the assumptions of our predictive model.

3.2 Initial and boundary conditions

Table 1 shows the initial conditions in the FF, while Table 2 the boundary conditions of the model for the entire working environment.

Table 1: Initial conditions in the FF

| | |
|-----------------------------------------------|------------------------------|
| Initial indoor oxygen concentration in the FF | $C_{O_2,FF}(0) = C_{O_2}(0)$ |
|-----------------------------------------------|------------------------------|

| | |
|-------------------------------------------|------------------------------|
| Initial moles of indoor oxygen in the FF | $n_{O_2,FF}(0) = n_{O_2}(0)$ |
| Initial indoor temperature in the FF | $T_{FF}(0) = T_{we}(0)$ |
| Initial indoor pressure in the FF | $p_{FF}(0) = p_{we}(0)$ |
| Initial indoor air composition in the FF: | |
| - initial indoor nitrogen concentration | $C_{N_2,FF}(0) = C_{N_2}(0)$ |
| - initial indoor argon concentration | $C_{Ar,FF}(0) = C_{Ar}(0)$ |
| - initial indoor helium concentration | $C_{He,FF}(0) = C_{He}(0)$ |
| - ... | ... |
| - initial indoor i-th gas concentration | $C_{i,FF}(0) = C_i(0)$ |

Table 2: Boundary conditions for the working environment

| | |
|----------------------------------|-----------------|
| Outdoor oxygen concentration | $C_{O_2,oe}(t)$ |
| Outdoor temperature | $T_{oe}(t)$ |
| Outdoor pressure | $p_{oe}(t)$ |
| Outdoor air composition: | |
| - outdoor nitrogen concentration | $C_{N_2,oe}(t)$ |
| - outdoor argon concentration | $C_{Ar,oe}(t)$ |
| - outdoor helium concentration | $C_{He,oe}(t)$ |
| - ... | ... |
| - outdoor i-th gas concentration | $C_{i,oe}(t)$ |

3.3 Mathematical formulation

Figure 1 depicts a generic working environment with the NF and the FF, and the indication of the different flows of oxygen due to releases, and to forced and natural ventilation.

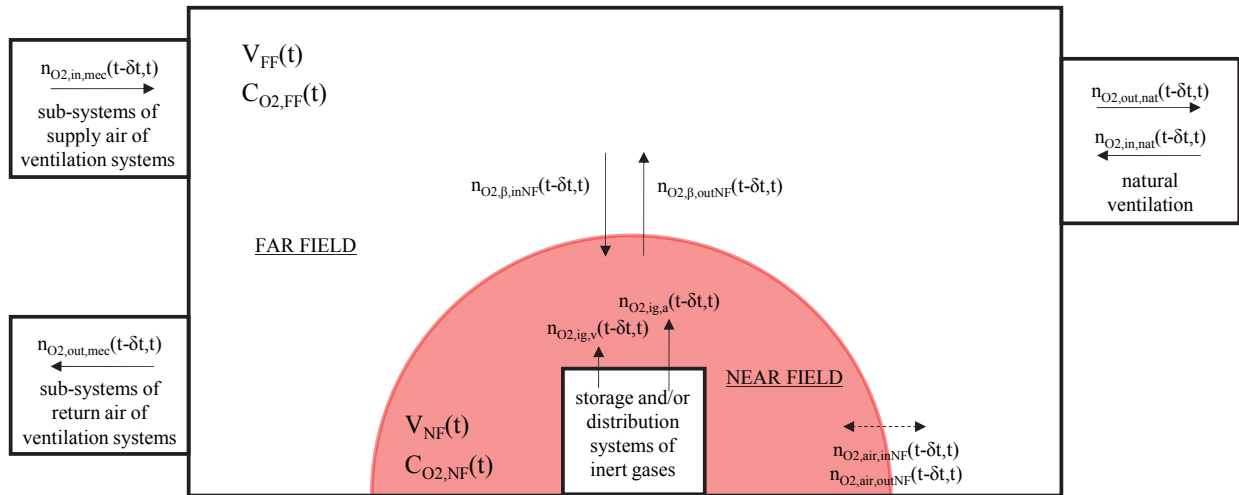


Figure 1: A generic working environment with the two boxes, and the indication of all the flows of oxygen moles

Applying the law of conservation of mass in the time interval $(t-\delta t, t)$ and considering only the oxygen in the NF and in the FF, we obtain Eq. (1) and Eq. (2), respectively. These equations represent the balances of moles of oxygen respectively in the NF and in the FF in the time interval $(t-\delta t, t)$.

$$n_{O_2,NF}(t) = n_{O_2,NF}(t-\delta t) + n_{O_2,ig,v}(t-\delta t, t) + n_{O_2,ig,a}(t-\delta t, t) + n_{O_2,air}(t-\delta t, t) + n_{O_2,\beta,inNF}(t-\delta t, t) - n_{O_2,\beta,outNF}(t-\delta t, t) \quad (1)$$

$$n_{O_2,FF}(t) = n_{O_2,FF}(t-\delta t) + n_{O_2,in,mec}(t-\delta t, t) - n_{O_2,out,mec}(t-\delta t, t) + n_{O_2,nat}(t-\delta t, t) - n_{O_2,air}(t-\delta t, t) - n_{O_2,\beta,inNF}(t-\delta t, t) + \quad (2)$$

As shown in Eq. (1), storage and/or distribution systems of inert gases can also release oxygen because it represents one of the impurities potentially present in the inert gases themselves. Therefore, $n_{O_2,ig,v}(t-\delta t, t)$ indicates the moles (n) of oxygen (O_2) contained in a flow of inert gas (ig) voluntarily (v) released into the NF between $t-\delta t$ and t . Similarly, $n_{O_2,ig,a}(t-\delta t, t)$ indicates the moles (n) of oxygen (O_2) contained in a flow of inert gas (ig) accidentally (a) released into the NF between $t-\delta t$ and t .

As a consequence, the total number of moles (oxygen, and different substances and gases) in the NF and in the FF at the instant t are estimated in Eq. (3) and in Eq. (4), respectively.

$$n_{NF}(t) = n_{NF}(t-\delta t) + n_{ig,v}(t-\delta t, t) + n_{ig,a}(t-\delta t, t) + n_{air}(t-\delta t, t) + n_{\beta,inNF}(t-\delta t, t) - n_{\beta,outNF}(t-\delta t, t) = \quad (3)$$

$$= n_{NF}(t-\delta t) + n_{ig,v}(t-\delta t, t) + n_{ig,a}(t-\delta t, t) + n_{air}(t-\delta t, t)$$

$$\begin{aligned} n_{FF}(t) &= n_{FF}(t-\delta t) + n_{in,mec}(t-\delta t, t) - n_{out,mec}(t-\delta t, t) + n_{nat}(t-\delta t, t) - n_{air}(t-\delta t, t) - n_{\beta,inNF}(t-\delta t, t) + n_{\beta,outNF}(t-\delta t, t) = \\ &= n_{FF}(t-\delta t) + n_{in,mec}(t-\delta t, t) - n_{out,mec}(t-\delta t, t) + n_{nat}(t-\delta t, t) - n_{air}(t-\delta t, t) \end{aligned} \quad (4)$$

Note that in Eq. (3) and in Eq. (4) the terms referred to the interzonal exchanges can be deleted because equal (considering the total moles).

The terms in Eq. (3) are related to: (1) the number of moles in the NF at the instant previous to the one being analysed, (2) the number of moles due to voluntary releases of inert gases, (3) the number of moles due to accidental releases of inert gases, and (4) the number of moles due to the expansion or the reduction of the NF for assuring a limit value for the oxygen concentration in the NF.

The terms in Eq. (4) are related to: (1) the number of moles in the FF at the instant previous to the one being analysed, (2) the number of moles due to the air introduced into the working environment by supply air sub-systems of ventilation systems, (3) the number of moles due to the air drawn from the working environment by return air sub-systems of ventilation systems, (4) the number of moles due to the air introduced into or drawn from the working environment in a natural way through the phenomenon of natural ventilation, (5) the number of moles due to the reduction or the expansion of the NF for assuring a limit value for the oxygen concentration in the NF.

3.3.1 Inputs of the predictive model

We define our model in order to exploit data that are typically available to the risk assessor. In particular, the model requires as inputs the entire volume of the working environment (V_{we}), its free ($V_{we,f}$) and occupied ($V_{we,occ}$) volumes. Furthermore, the safety manager has to know the initial conditions of indoor air (i.e. pressure, temperature, and composition), and the conditions of outdoor air (i.e. pressure, temperature, and composition). The outdoor pressure at a certain altitude can be estimated according to the relationships reported in the ISO 2533 standard (ISO, 1975).

With regard to ventilation systems, the model needs information about flow rate, composition, and temperature of possible air flows introduced into the working environment by supply air sub-systems of ventilation systems, and about flow rate of possible air flows drawn from the working environment by return air sub-systems of ventilation systems. Reliability analysis for both supply air and return air sub-systems are fundamental.

Substances and mixtures released and used in the working environment must be characterised in terms of flow rate, composition, temperature, and pressure. Also a reliability analysis of storage and/or distribution systems is required. Another input required for estimating the volume of the NF is the limit value for the oxygen concentration ($C_{O2,NF}(t)$), which can be set by the risk assessor. This parameter can be a constant value or vary over time: in certain time intervals the risk assessor may set a greater (and therefore more precautionary) limit value for the oxygen concentration, while in other one thanks to the presence of safety measures and mitigation controls (e.g. Personal Protective Equipment).

The risk assessor may also set the value of the atmospheric oxygen partial pressure ($pp_{O2,NF}(t)$), converting this indicator in an oxygen concentration by volume thanks to Eq. (5):

$$C_{O2,NF}(t) = \frac{pp_{O2,NF}(t)}{p_{we}(t)} \quad (5)$$

In the literature, the risk assessor can found several examples of ODH definitions that can be exploited for setting the limit value of oxygen; some of them are summarised in Stefana et al. (2015). Furthermore, risk assessors and safety managers might apply the model using values lower than the ones suggested in ODH definitions. In this case, they may exploit tables available in the literature that show the different symptoms and physiological effects at different concentrations by volume. An overview of this information is provided in Stefana et al. (2016).

3.3.2 Equations at the instant of time $t-\delta t$

For each constituent of indoor air (i.e. oxygen, pure inert gases, impurities), we can convert input data about the instant of time $t-\delta t$ in moles thanks to the application of the ideal gas law. Consequently, we can estimate the number of moles of the NF and of the FF at the beginning of each considered time interval. For example, Eq. (6) and Eq. (7) represent the moles of oxygen in the instant of time $t-\delta t$ in the NF and in the FF, respectively:

$$n_{O2,NF}(t-\delta t) = \frac{p_{NF}(t-\delta t)V_{NF}(t-\delta t)}{RT_{NF}(t-\delta t)} C_{O2,NF}(t-\delta t) \quad (6)$$

$$n_{O2,FF}(t-\delta t) = \frac{p_{FF}(t-\delta t)V_{FF}(t-\delta t)}{RT_{FF}(t-\delta t)} C_{O2,FF}(t-\delta t) \quad (7)$$

Note that $p_{NF}(t-\delta t)$ is equal to $p_{FF}(t-\delta t)$, and equal to $p_{we}(t-\delta t)$. Similarly, $T_{NF}(t-\delta t)$ is equal to $T_{FF}(t-\delta t)$, and equal to $T_{we}(t-\delta t)$.

3.3.3 Equations for the time interval $(t-\delta t, t)$

After the estimation of the moles of the NF and of the FF at the instant of time $t-\delta t$, we have to estimate other terms of Eq. (1), Eq. (2), Eq. (3), and Eq. (4). In particular, we exploit the ideal gas law with data about volumetric flow rates, volume fractions, pressure, and temperature of each flow released into, introduced into, and drawn from the working environment. In addition, we use some binary variables in order to understand which gases are stored in a specific storage and/or distribution system ($k_{s,i}$), if the s -th supply air sub-system of ventilation systems introduces air into the working environment ($k_{in,mec;s}$), or if the s -th return air sub-system of ventilation systems draws air from the working environment ($k_{out,mec;s}$).

3.3.3.1 Near Field

As shown in Eq. (1) and Eq. (3), the NF composition can change because of inert gases released voluntarily and/or accidentally, the interzonal airflow, and the air that has to move from the FF to the NF, or vice versa, for assuring a limit value for the oxygen concentration in the NF.

In order to estimate the moles of oxygen, of main pure inert gas, of each other pure inert gas, and of each other impurity related to voluntary and/or accidental releases of inert gases, we can exploit equations reported in Table 3, as already addressed in Stefana et al. (2016).

Table 3: Moles of each constituent of flows of inert gases released voluntarily and accidentally into the NF

| Type of flow | Constituent | Moles (mol) | |
|------------------------------------|---------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Voluntary releases of inert gases | Oxygen | $n_{O_2,ig,v}(t-\delta t, t) = \sum_{s=1}^S \sum_{i=1}^I \left\{ k_{s,i} \frac{p_{ig,v}(t-\delta t) \phi_{O_2,ig,v,s,i} \int_{t-\delta t}^t \dot{Q}_{ig,v,s,i}(t) dt}{RT_{ig,v}(t-\delta t)} Rel_{ig,v,s,i}(t-\delta t) \right\}$ | (8) |
| | Main pure inert gas | $n_{x,ig,v}(t-\delta t, t) = \sum_{s=1}^S \sum_{i=1}^I \left\{ k_{s,i} \frac{p_{ig,v}(t-\delta t) \phi_{x,ig,v,s,i} \int_{t-\delta t}^t \dot{Q}_{ig,v,s,i}(t) dt}{RT_{ig,v}(t-\delta t)} Rel_{ig,v,s,i}(t-\delta t) \right\}$ | (9) |
| | Each other pure inert gas | $n_{y,ig,v}(t-\delta t, t) = \sum_{s=1}^S \sum_{i=1}^I \left\{ k_{s,i} \frac{p_{ig,v}(t-\delta t) \phi_{y,ig,v,s,i} \int_{t-\delta t}^t \dot{Q}_{ig,v,s,i}(t) dt}{RT_{ig,v}(t-\delta t)} Rel_{ig,v,s,i}(t-\delta t) \right\}$ | (10) |
| | Each other impurity | $n_{imp,ig,v}(t-\delta t, t) = \sum_{s=1}^S \sum_{i=1}^I \left\{ k_{s,i} \frac{p_{ig,v}(t-\delta t) \phi_{imp,ig,v,s,i} \int_{t-\delta t}^t \dot{Q}_{ig,v,s,i}(t) dt}{RT_{ig,v}(t-\delta t)} Rel_{ig,v,s,i}(t-\delta t) \right\}$ | (11) |
| Accidental releases of inert gases | Oxygen | $n_{O_2,ig,a}(t-\delta t, t) = \sum_{s=1}^S \sum_{j=1}^J \sum_{i=1}^I \left\{ k_{s,i} \frac{p_{ig,a}(t-\delta t) \phi_{O_2,ig,a,s,i} \int_{t-\delta t}^t \dot{Q}_{ig,a,s,j,i}(t) dt}{RT_{ig,a}(t-\delta t)} P_{ig,a,s,j,i}(t-\delta t) \right\}$ | (12) |
| | Main pure inert gas | $n_{x,ig,a}(t-\delta t, t) = \sum_{s=1}^S \sum_{j=1}^J \sum_{i=1}^I \left\{ k_{s,i} \frac{p_{ig,a}(t-\delta t) \phi_{x,ig,a,s,i} \int_{t-\delta t}^t \dot{Q}_{ig,a,s,j,i}(t) dt}{RT_{ig,a}(t-\delta t)} P_{ig,a,s,j,i}(t-\delta t) \right\}$ | (13) |
| | Each other pure inert gas | $n_{y,ig,a}(t-\delta t, t) = \sum_{s=1}^S \sum_{j=1}^J \sum_{i=1}^I \left\{ k_{s,i} \frac{p_{ig,a}(t-\delta t) \phi_{y,ig,a,s,i} \int_{t-\delta t}^t \dot{Q}_{ig,a,s,j,i}(t) dt}{RT_{ig,a}(t-\delta t)} P_{ig,a,s,j,i}(t-\delta t) \right\}$ | (14) |
| | Each other impurity | $n_{imp,ig,a}(t-\delta t, t) = \sum_{s=1}^S \sum_{j=1}^J \sum_{i=1}^I \left\{ k_{s,i} \frac{p_{ig,a}(t-\delta t) \phi_{imp,ig,a,s,i} \int_{t-\delta t}^t \dot{Q}_{ig,a,s,j,i}(t) dt}{RT_{ig,a}(t-\delta t)} P_{ig,a,s,j,i}(t-\delta t) \right\}$ | (15) |

We model voluntary and accidental releases introducing proper multiplicative factors (dimensionless) related to the field of reliability analysis. In particular, a voluntary release depends on the reliability (Rel) of storage and/or distribution systems. In particular, this reliability is the probability that a certain entity or component of this type of system fulfils the required functions, assuring the release. The reliability of a storage and/or distribution system can be equal: (1) to 1 and thus the system is completely and correctly working, and the release flow rate is equal to the set and desired one; (2) to a value between 0 (excluded) and 1, and so this system partially works, and the release flow rate decreases; and (3) to 0 and thus there are no voluntary releases because of a failure of this system. On the contrary, an accidental release depends on the probability that a storage and/or distribution system fails (due to equipment failures and/or human errors) causing an unwanted release. This type of release can be continuous and mostly uncontrolled, and can also cause oxygen depletion in the working environment. In general, when the probability of accidental releases increases, the expected flow of inert gases increases, and the indoor oxygen concentration decreases. The probability set to 1 represents the worst case, in which the flow of released inert gas is maximum.

With regard to the interzonal airflow, we have defined two variables. The first is consistent with the definition of β given by Nicas (1996) and used in other NF-FF models (e.g. Nicas et al. (2006)). Indeed, it represents the interzonal volumetric airflow rate (for us: $\dot{\beta}$, in $m^3 s^{-1}$) between the NF and FF. The second is the interzonal volume (for us: β , in m^3) between the NF and FF. Eq. (16) and Eq. (17) propose the definition of β and of $\dot{\beta}$, respectively.

$$\beta(t-\delta t, t) = \int_{t-\delta t}^t \dot{\beta}(t) dt \quad (16)$$

$$\dot{\beta}(t) = \frac{1}{2} \text{FSA}(t) s(t) \quad (17)$$

The interzonal airflow rate $\dot{\beta}$ is time-dependent because in every time instant the volume of the NF varies and thus also the free surface area changes, modifying the value of β . In Eq. (17) FSA is the free surface area of the NF (m^2), and s the random airspeed at the boundary of the near field (m s^{-1}). The random airspeed at the boundary of the near field can be set by the risk assessor. Some advice on how to select values for s in order to calculate the interzonal airflow rate is provided by Sahmel et al. (2009) that review 16 two-zone modelling papers.

If at the instant of time $t-\delta t$ there is no NF, $\text{FSA}(t-\delta t)$ is equal to 0 and thus also $\beta(t-\delta t, t)$. Furthermore, there are no interzonal exchanges if the volume of the NF is equal to the volume of the working environment because the FF vanishes. On the contrary, if the NF is present at the previous instant, the moles due to interzonal airflow rate can be estimated through Eq. (18).

$$n_{\beta, \text{inNF}}(t-\delta t, t) = n_{\beta, \text{outNF}}(t-\delta t, t) = \frac{p_{\text{we}}(t-\delta t) \beta(t-\delta t, t)}{RT_{\text{we}}(t-\delta t)} \quad (18)$$

As a consequence, we can calculate the number of moles (in total and for each constituent of indoor air) related to β . The moles related to β flow in both directions: from the FF to the NF (and thus entering the NF with the air composition of the FF), and from the NF to the FF (thus leaving the NF with the air composition of the NF). For example, in the case of oxygen, the moles are determined applying Eq. (19) and Eq. (20).

$$n_{\text{O}_2, \beta, \text{inNF}}(t-\delta t, t) = n_{\beta, \text{inNF}}(t-\delta t, t) C_{\text{O}_2, \text{FF}}(t-\delta t) \quad (19)$$

$$n_{\text{O}_2, \beta, \text{outNF}}(t-\delta t, t) = n_{\beta, \text{outNF}}(t-\delta t, t) C_{\text{O}_2, \text{NF}}(t-\delta t) \quad (20)$$

In order to complete the balances of moles in the NF, we calculate $n_{\text{air}}(t-\delta t, t)$, which guides the necessary expansion or reduction of the NF volume in the next time step. Indeed, this parameter represents the air that has to move from the FF to the NF, or vice versa, for assuring a limit value for the oxygen concentration in the NF in the next time instant. In particular, $n_{\text{air}}(t-\delta t, t)$ guides the expansion of the NF volume in the next time step when the NF does not contain a number of oxygen moles that guarantee the limit value for the oxygen concentration and thus the volume of the NF has to increase. On the contrary, $n_{\text{air}}(t-\delta t, t)$ guides the reduction of the NF volume in the next time step when the NF already contains a sufficient level of oxygen: in the NF there are a number of oxygen moles greater than those necessary to ensure the limit value for the oxygen concentration and thus the NF volume has to decrease. Therefore, at each time instant it is necessary to understand if the moles of oxygen in the NF due to the ones present in the previous instant, the inert gas releases, and the interzonal airflow are such as to assure a limit value for the oxygen concentration.

In order to estimate $n_{\text{air}}(t-\delta t, t)$, we define a parameter (for sake of brevity, called $\tilde{C}_{\text{O}_2, \text{NF}}(t)$) that is estimated thanks to Eq. (21). We obtain this $\tilde{C}_{\text{O}_2, \text{NF}}(t)$ thanks to the ratio between $\tilde{n}_{\text{O}_2, \text{NF}}(t)$ and $\tilde{n}_{\text{NF}}(t)$, which are calculated by equalling $n_{\text{O}_2, \text{air}}(t-\delta t, t)$ and $n_{\text{air}}(t-\delta t, t)$ to 0 in Eq. (1) and Eq. (3).

$$\tilde{C}_{\text{O}_2, \text{NF}}(t) = \frac{\tilde{n}_{\text{O}_2, \text{NF}}(t)}{\tilde{n}_{\text{NF}}(t)} = \frac{n_{\text{O}_2, \text{NF}}(t-\delta t) + n_{\text{O}_2, \text{ig}, v}(t-\delta t, t) + n_{\text{O}_2, \text{ig}, a}(t-\delta t, t) + n_{\text{O}_2, \beta, \text{inNF}}(t-\delta t, t) - n_{\text{O}_2, \beta, \text{outNF}}(t-\delta t, t)}{n_{\text{NF}}(t-\delta t) + n_{\text{ig}, v}(t-\delta t, t) + n_{\text{ig}, a}(t-\delta t, t)} \quad (21)$$

The tilde in Eq. (21) means that the oxygen concentration is approximated because of the lack of moles $n_{\text{air}}(t-\delta t, t)$. Indeed, Eq. (21) allows to estimate the new value of the oxygen concentration (temporary value) in the NF at the instant t , after releases of inert gases and the interzonal airflows, and before the possible movement of air from the FF to the NF, or vice versa, for assuring a limit value for the oxygen concentration.

Furthermore, we can write Eq. (22):

$$C_{\text{O}_2, \text{NF}}(t) = \frac{n_{\text{O}_2, \text{NF}}(t)}{n_{\text{NF}}(t)} = \frac{\tilde{n}_{\text{O}_2, \text{NF}}(t) + n_{\text{O}_2, \text{air}}(t-\delta t, t)}{\tilde{n}_{\text{NF}}(t) + n_{\text{air}}(t-\delta t, t)} \quad (22)$$

As underlined in Section 3.3.1, the limit value for the oxygen concentration $C_{\text{O}_2, \text{NF}}(t)$ is an input of the predictive model.

Eq. (23) represents the difference between $C_{O_2,NF}(t)$ and $\tilde{C}_{O_2,NF}(t)$:

$$C_{O_2,NF}(t) - \tilde{C}_{O_2,NF}(t) = \frac{\tilde{n}_{NF}(t)n_{O_2,air}(t-\delta t, t) - \tilde{n}_{O_2,NF}(t)n_{air}(t-\delta t, t)}{\tilde{n}_{NF}(t)n_{NF}(t)} \quad (23)$$

Eq. (23) also allows to make explicit the term $n_{air}(t-\delta t, t)$, according to Eq. (24):

$$n_{air}(t-\delta t, t) = \frac{[C_{O_2,NF}(t) - \tilde{C}_{O_2,NF}(t)]\tilde{n}_{NF}(t)n_{NF}(t)}{\tilde{n}_{NF}(t)C_{O_2,NForFF}(t-\delta t) - \tilde{n}_{O_2,NF}(t)} \quad (24)$$

where the term $C_{O_2,NForFF}$ represents the oxygen concentration that must multiply $n_{air}(t-\delta t, t)$ in order to obtain the moles of oxygen related to this flow of air moving from the FF to the NF, or vice versa, as underlined in Eq. (25).

$$n_{O_2,air}(t-\delta t, t) = C_{O_2,NForFF}(t-\delta t)n_{air}(t-\delta t, t) \quad (25)$$

As a consequence, $C_{O_2,NForFF}$ can indicate the oxygen concentration of the FF (if $b_{air,inNF} = 1$) or the one of the NF (if $b_{air,outNF} = 1$) in the previous instant time. In particular, introducing two binary variables that state if these moles proceed from the FF towards the NF, $b_{air,inNF}$, or from the NF towards the FF, $b_{air,outNF}$:

$$\begin{cases} b_{air,inNF}, b_{air,outNF} \text{ integer} \\ b_{air,inNF}, b_{air,outNF} \in \{0,1\} \\ b_{air,inNF} + b_{air,outNF} \leq 1 \end{cases}$$

we can write Eq. (26):

$$C_{O_2,NForFF}(t-\delta t) = b_{air,inNF}C_{O_2,FF}(t-\delta t) + b_{air,outNF}C_{O_2,NF}(t-\delta t) \quad (26)$$

According to the value of $\tilde{C}_{O_2,NF}(t)$, we have three cases:

- if $\tilde{C}_{O_2,NF}(t) = C_{O_2,NF}(t)$, then both $b_{air,inNF}$ and $b_{air,outNF}$ are equal to 0, and $n_{air}(t-\delta t, t)$ is equal to 0 (this means that the NF already has an oxygen concentration exactly equal to the limit value for the oxygen concentration, and therefore it is not necessary to increase or reduce its volume);
- if $\tilde{C}_{O_2,NF}(t) < C_{O_2,NF}(t)$, then $b_{air,inNF}$ is equal to 1 ($b_{air,outNF} = 0$) and this means that the NF increases in volume in order to achieve the limit value for the oxygen concentration; in this case $n_{O_2,air}(t-\delta t, t)$ and $n_{air}(t-\delta t, t)$ have positive values;
- if $\tilde{C}_{O_2,NF}(t) > C_{O_2,NF}(t)$, then $b_{air,outNF}$ is equal to 1 ($b_{air,inNF} = 0$) and this means that the NF is reduced in volume because the oxygen concentration in the NF (without the contribution of additional air) is greater than the limit value for the oxygen concentration; in this case $n_{O_2,air}(t-\delta t, t)$ and $n_{air}(t-\delta t, t)$ have negative values.

By using the following system of equations:

$$\begin{cases} n_{air}(t-\delta t, t) = \frac{[C_{O_2,NF}(t) - \tilde{C}_{O_2,NF}(t)]\tilde{n}_{NF}(t)n_{NF}(t)}{\tilde{n}_{NF}(t)C_{O_2,NForFF}(t-\delta t) - \tilde{n}_{O_2,NF}(t)} \\ n_{NF}(t) - n_{air}(t-\delta t, t) = \tilde{n}_{NF}(t) \end{cases}$$

we obtain the total number of moles in the NF thanks to Eq. (27), and $n_{air}(t-\delta t, t)$ by using the second equation of the system above.

$$n_{NF}(t) = \frac{\tilde{n}_{NF}(t)[\tilde{n}_{NF}(t)C_{O_2,NForFF}(t-\delta t) - \tilde{n}_{O_2,NF}(t)]}{\tilde{n}_{NF}(t)C_{O_2,NForFF}(t-\delta t) - \tilde{n}_{O_2,NF}(t) - \tilde{n}_{NF}(t)[C_{O_2,NF}(t) - \tilde{C}_{O_2,NF}(t)]} \quad (27)$$

In Appendix 2 we report the mathematical demonstration of above equations for calculating $n_{air}(t-\delta t, t)$ and $n_{NF}(t)$. After determining $n_{air}(t-\delta t, t)$, we can calculate the moles of its constituents; for example, the moles of oxygen related to this airflow between the NF and the FF can be estimated thanks to Eq. (28) or Eq. (29).

$$n_{O_2,air,inNF}(t-\delta t, t) = b_{air,inNF}n_{air}(t-\delta t, t)C_{O_2,FF}(t-\delta t) \quad (28)$$

$$n_{O_2,air,outNF}(t-\delta t,t) = b_{air,outNF} n_{air}(t-\delta t,t) C_{O_2,NF}(t-\delta t) \quad (29)$$

3.3.3.2 Far Field

Thanks to the equations reported in Table 4 and already addressed in Stefana et al. (2016), the risk assessor can estimate the moles of forced ventilation airflow (supply and return air) in terms of oxygen, each pure inert gas, and each impurity.

Table 4: Moles of each air constituent introduced into and/or drawn from the FF

| Type of flow | Constituent | Moles (mol) | |
|-----------------------------------------|---------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Forced ventilation airflow (supply air) | Oxygen | $n_{O_2,in,mec}(t-\delta t,t) = \sum_{s=1}^S \left\{ k_{in,mec;s} \frac{p_{in,mec}(t-\delta t) C_{O_2,in,mec;s}(t-\delta t) \int_{t-\delta t}^t \dot{Q}_{in,mec;s}(t) dt}{RT_{in,mec}(t-\delta t)} Rel_{in,mec;s}(t-\delta t) \right\}$ | (30) |
| | Each pure inert gas | $n_{y,in,mec}(t-\delta t,t) = \sum_{s=1}^S \left\{ k_{in,mec;s} \frac{p_{in,mec}(t-\delta t) C_{y,in,mec;s}(t-\delta t) \int_{t-\delta t}^t \dot{Q}_{in,mec;s}(t) dt}{RT_{in,mec}(t-\delta t)} Rel_{in,mec;s}(t-\delta t) \right\}$ | (31) |
| | Each impurity | $n_{imp,in,mec}(t-\delta t,t) = \sum_{s=1}^S \left\{ k_{in,mec;s} \frac{p_{in,mec}(t-\delta t) C_{imp,in,mec;s}(t-\delta t) \int_{t-\delta t}^t \dot{Q}_{in,mec;s}(t) dt}{RT_{in,mec}(t-\delta t)} Rel_{in,mec;s}(t-\delta t) \right\}$ | (32) |
| Forced ventilation airflow (return air) | Oxygen | $n_{O_2,out,mec}(t-\delta t,t) = \sum_{s=1}^S \left\{ k_{out,mec;s} \frac{p_{we}(t-\delta t) C_{O_2}(t-\delta t) \int_{t-\delta t}^t \dot{Q}_{out,mec;s}(t) dt}{RT_{we}(t-\delta t)} Rel_{out,mec;s}(t-\delta t) \right\}$ | (33) |
| | Each pure inert gas | $n_{y,out,mec}(t-\delta t,t) = \sum_{s=1}^S \left\{ k_{out,mec;s} \frac{p_{we}(t-\delta t) C_y(t-\delta t) \int_{t-\delta t}^t \dot{Q}_{out,mec;s}(t) dt}{RT_{we}(t-\delta t)} Rel_{out,mec;s}(t-\delta t) \right\}$ | (34) |
| | Each impurity | $n_{imp,out,mec}(t-\delta t,t) = \sum_{s=1}^S \left\{ k_{out,mec;s} \frac{p_{we}(t-\delta t) C_{imp}(t-\delta t) \int_{t-\delta t}^t \dot{Q}_{out,mec;s}(t) dt}{RT_{we}(t-\delta t)} Rel_{out,mec;s}(t-\delta t) \right\}$ | (35) |

The moles introduced into or drawn from the working environment with natural ventilation can be calculated adapting the formulas reported in Stefana et al. (2016) and considering as internal conditions the ones of the FF. We have supposed that natural ventilation, infiltration, and exfiltration are driven only by pressure difference inside and outside the working environment. The indoor pressure can vary over time because of several releases and flows of forced ventilation, while the outdoor pressure can change between $t-\delta t$ and t due to external phenomena. The flow of natural ventilation balances this pressure difference in order to maintain the constant equilibrium between the indoor and the outdoor pressures. Therefore, at the steady state, we have assumed that the indoor pressure is equal to the outdoor pressure, thanks to the natural ventilation.

In particular, Eq. (36) estimates the moles of natural ventilation introduced into or drawn from the FF during the time interval $(t-\delta t,t)$:

$$n_{nat}(t-\delta t,t) = b_{in,nat} \frac{[p_{oe}(t) - \tilde{p}_{we}(t)]V_{we,f}}{RT_{oe}(t-\delta t)} + b_{out,nat} \frac{[p_{oe}(t) - \tilde{p}_{we}(t)]V_{we,f}}{RT_{we}(t-\delta t)} \quad (36)$$

where $\tilde{p}_{we}(t)$ is the temporary value of the pressure of the working environment at the time t (after releases of inert gases, airflows introduced into or drawn from the working environment by ventilation systems, and before the possible phenomenon of the natural ventilation).

In addition, in Eq. (36) there are two binary variables that state if these moles proceed from the inside towards the outside, $b_{out,nat}$, or from the outside towards the inside, $b_{in,nat}$:

$$\begin{cases} b_{in,nat}, b_{out,nat} & \text{integer} \\ b_{in,nat}, b_{out,nat} & \in \{0,1\} \\ b_{in,nat} + b_{out,nat} & \leq 1 \end{cases}$$

whose values are automatically set:

$$\begin{cases} b_{in,nat} = 1 & \text{if } \tilde{p}_{we}(t) < p_{oe}(t) \\ b_{in,nat} = 0 & \text{otherwise} \\ b_{out,nat} = 1 & \text{if } \tilde{p}_{we}(t) > p_{oe}(t) \\ b_{out,nat} = 0 & \text{otherwise} \end{cases}$$

The moles of oxygen introduced into or drawn from the FF with natural ventilation are estimated through Eq. (37).

$$n_{O_2,nat}(t-\delta t,t)=b_{in,nat}\frac{[p_{oe}(t)-\tilde{p}_{we}(t)]V_{we,f}}{RT_{oe}(t-\delta t)}C_{O_2,oe}(t-\delta t)+b_{out,nat}\frac{[p_{oe}(t)-\tilde{p}_{we}(t)]V_{we,f}}{RT_{we}(t-\delta t)}C_{O_2,FF}(t-\delta t) \quad (37)$$

The flow of natural ventilation also influences the temperature of the working environment at the time instant t , which is calculated through Eq. (38):

$$T_{we}(t) = \frac{n_{we}(t-\delta t)T_{we}(t-\delta t)p_{we}(t)}{p_{we}(t-\delta t)n_{we}(t)} \quad (38)$$

Finally, the moles of air $n_{air}(t-\delta t,t)$ and the interzonal airflow rate are determined according to the equations of Section 3.3.3.1 with the sign of the balance of the FF (Eq. (2) and Eq. (4)).

3.3.4 Outputs of the model

The main output of the model is the volume of the NF at the time instant t according to Eq. (39). As a consequence, we can determine the volume of the FF at instant t with Eq. (40).

$$V_{NF}(t) = \frac{n_{NF}(t)RT_{NF}(t)}{p_{NF}(t)} = \frac{n_{NF}(t)RT_{we}(t)}{p_{we}(t)} \quad (39)$$

$$V_{FF}(t) = V_{we,f} - V_{NF}(t) \quad (40)$$

In order to apply properly Eq. (39), note that a change of the outdoor pressure causes a variation of the total number of moles in the working environment and of the volume of the NF, while the number of moles in the NF does not vary.

By applying the balances of oxygen reported in Eq. (1) and Eq. (2), we can also verify that the oxygen concentration in the NF is the one set by the risk assessor (i.e. the limit value for the oxygen concentration).

Another output of the model can be the distance of the worker from the release point. In some cases (when the limit value for the oxygen concentration is set according to the ODH definitions), this can be considered as a safety distance that the operator must keep to prevent the asphyxiation risk. According to the geometry chosen by the risk assessor for the NF, it can be estimated in a slightly different way. Indeed, in the case of NF hemisphere-shaped and centred on the release point, this distance is the radius of the hemisphere r and can be calculated through Eq. (41).

$$r(t) = \sqrt[3]{\frac{3 V_{NF}(t)}{2 \pi}} \quad (41)$$

Note that the distance depends on the time: at each instant the distance of the worker from the release point could change in order to prevent the asphyxiation risk.

Finally, the risk assessor can calculate the average oxygen concentration of the working environment through Eq. (42):

$$C_{O_2}(t) = \frac{C_{O_2,NF}(t)V_{NF}(t) + C_{O_2,FF}(t)V_{FF}(t)}{V_{we,f}} \quad (42)$$

4 Case studies

In order to evaluate the new NF-FF model, we applied it considering some case studies available in the literature. In all case studies, we predicted the volume of the NF assuming that this field has a hemispherical geometry.

Therefore, the distance between the worker and the release point is the radius of the hemisphere.

Times in the graphs (x-axis) are truncated when the NF volume reaches the volume of the working environment.

Indeed, when the volume of the NF becomes equal to the volume of the working environment the two zone model loses importance: in this case the NF coincides with the working environment, the FF vanishes, and as a consequence there are no interzonal exchanges between the two zones.

In all figures there are two y-axes, the left one represents the order of magnitude of the volume for the NF, while the one on the right the order of magnitude of the volume for the FF.

The common assumptions for applying our NF-FF model in the case studies proposed by Augustynowicz (1993), Bonfini et al. (2013), and Delaysen et al. (2001) are: $C_{N_2,we}(0) = C_{N_2,oe}(0) = 79\%$; $C_{O_2,we}(0) = C_{O_2,oe}(0) = 21\%$; $T_{we}(0) = T_{oe}(0) = 293.15\text{ K}$; $T_{ig,a}(0) = 293.15\text{ K}$; $P_{ig,a;s,j,i}(0) = 1$; $R = 8.314472\text{ J K}^{-1}\text{ mol}^{-1}$. We assumed that outdoor

parameters, such as pressure, temperature, and air composition, are constant in time. In addition, the released flow of inert gas is pure and thus does not contain oxygen, other pure inert gases, or other impurities. If not specified, we assumed the random airspeed at the boundary of the NF equal to 0.06 m s^{-1} , which is quoted as a reference value by several authors in the literature (e.g. Gaffney et al., 2008). Finally, for the sake of simplicity we supposed that at the initial time instant ($t = 0$) there is no NF, and thus both the initial NF volume and the initial moles of indoor oxygen in the NF are equal to 0. Indeed, at the time $t = 0$ the working environment coincides with the FF. If not specified, we supposed that $\delta t = 1 \text{ s}$.

4.1 Case study of Augustynowicz (1993)

The first case study to which we have applied our model is the one proposed by Augustynowicz (1993). He determines the oxygen concentration varying the flow rate of the release in a building containing helium located in U.S. Superconducting Super Collider Laboratory. In particular, Augustynowicz (1993) considers equipment such as helium compressors with oil skid, refrigerator and liquefier, distribution box, storage tanks, and penetration and connecting pipes. By assuming a helium flow rate equal to 1 kg s^{-1} for 1000 s, Figure 2 and Figure 3 point out the time trend of the volumes of the NF and of the FF, taking into account a limit value for the oxygen concentration equal to 17 % and 4 %, respectively. Note that an oxygen concentration of 4 % is very dangerous (it could cause death in a few minutes) from the point of view of ODH assessment, but it is an extreme case where we wanted to highlight the application of the model. The volume of the working environment useful for applying the model is equal to 2205 m^3 : Augustynowicz (1993) underlines that the volume of the building is equal to 2450 m^3 , with 10 % less for the volume of the equipment. In addition, $p_{we}(0) = p_{oe}(0) = 98920 \text{ Pa}$.

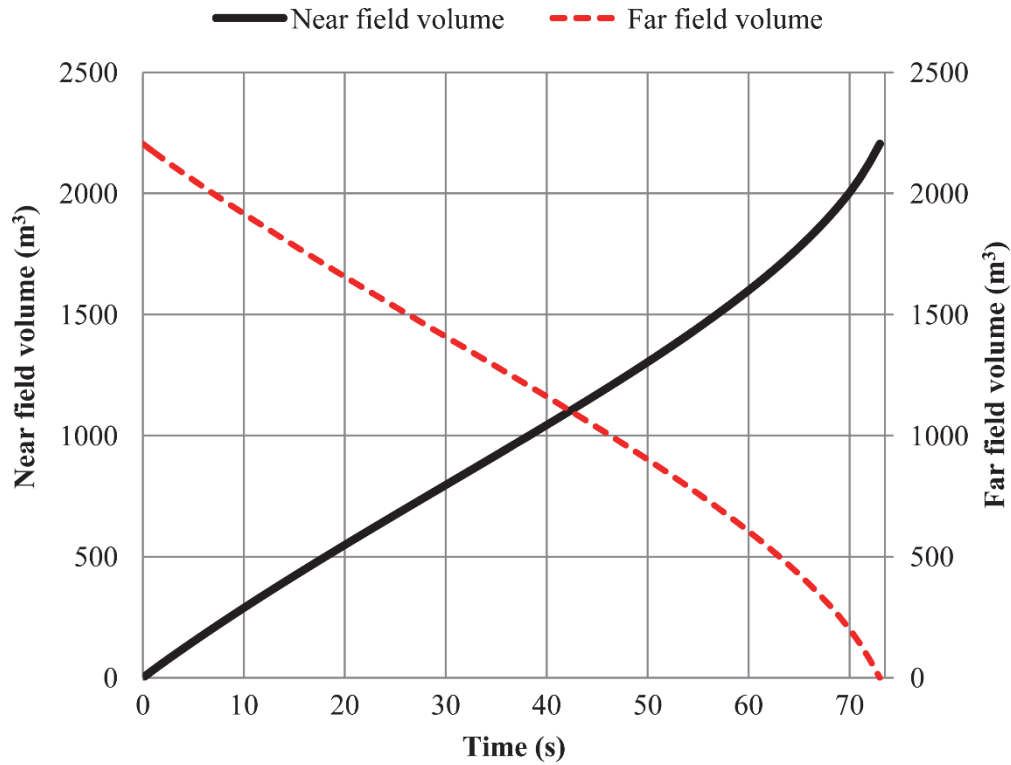


Figure 2: NF and FF volumes in the case study of Augustynowicz (1993), $C_{O_2,NF}(t) = 17 \%$

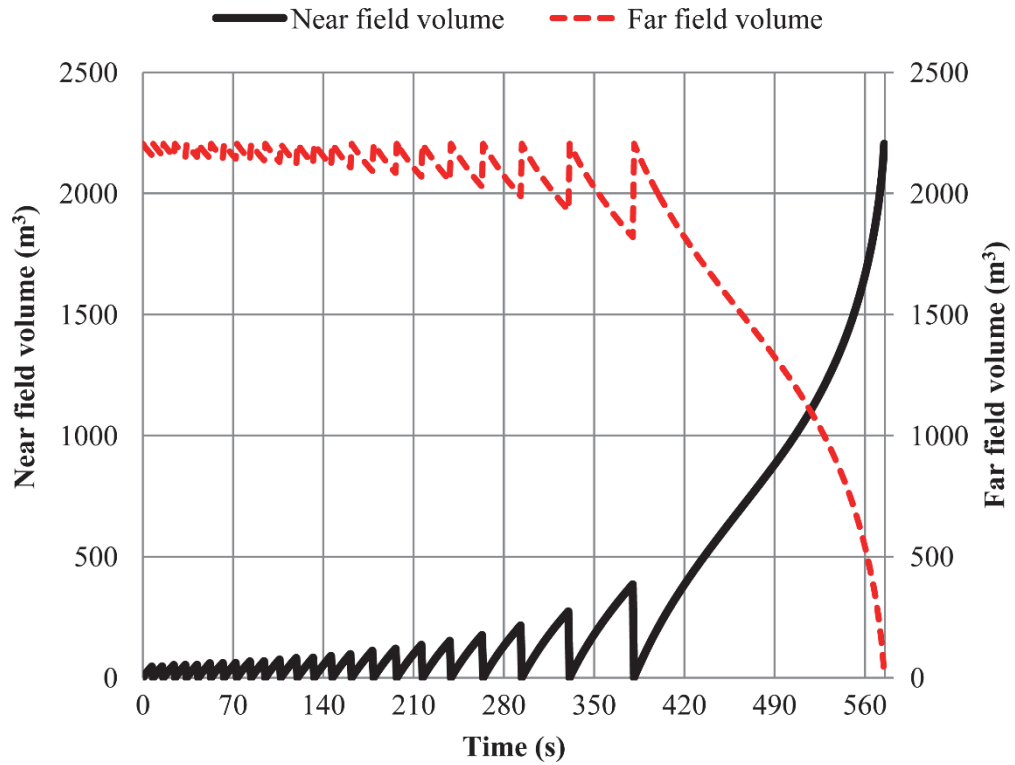


Figure 3: NF and FF volumes in the case study of Augustynowicz (1993), $C_{O_2,NF}(t) = 4\%$

As can be seen in Figure 2, after 73 s the NF is equal to the working environment. From this moment on, no FF exists anymore. Consequently, in 73 s the working environment has an oxygen concentration equal to the limit value for the oxygen concentration of 17 %. The radius of the hemisphere representing the NF varies during the time interval: for example, at $t = 25$ s it is equal to 6.85 m, while at $t = 50$ s to 8.54 m. In this scenario, ODH is severe and the risk assessor has to prevent the reduction of indoor oxygen level thanks to the adoption of some organisational and technical measures, and to define a proper emergency planning.

In the case of Figure 3 (with a lower limit value for the oxygen concentration than the one of Figure 2), the time required to achieve the equality between NF and working environment is greater and equal to 575 s. This result is expected: a reduction of the limit value for the oxygen concentration increases the time to create a working environment with that oxygen concentration (because much inert gas should be released). Unlike the previous case (Figure 2), the volume of the NF increases and comes back to zero several times. Indeed, the oxygen content in the previous instant time and the flows related to the release of an inert gas and interzonal flow make the oxygen concentration within the NF higher than the limit value for the fixed oxygen concentration. For example, in the time interval between 7 and 8 s, the flows related to the release of an inert gas and interzonal flow lead the oxygen concentration in the NF to about 4.022 %. Therefore, the flow rate of air (n_{air}) has then to extract air that proceeds from the NF to the FF in order to guarantee exactly the limit value for the oxygen concentration in the NF (in this case, 4 %). For the assumption of perfect mixing in the NF, n_{air} has an oxygen concentration equal to 4.022 % and thus no air flow with this oxygen concentration is able to reduce the oxygen concentration in the NF to 4 %. As a consequence, the flow of air n_{air} will extract a quantity of air that cancels temporarily the volume of the NF. The radius of the NF constantly changes during the simulation: for instance, at $t = 119$ s it is equal to 3.39 m, at $t = 330$ s to 5.08 m, and at $t = 550$ s to 8.90 m.

4.2 Case study of Bonfini et al. (2013)

Bonfini et al. (2013) present an oxygen deficiency case study in a box used as a storage area and located in the underground laboratories of the Italian Gran Sasso Nuclear Physics Laboratory. Their case study compares the trends of oxygen concentration obtained through the application of their theoretical approach based on the version published in 2009 of the model of Fermilab (Fermilab, 2009), a real test, and a Computational Fluid Dynamics (CFD) simulation. With reference to this case, the NF-FF model provides the results depicted in Figure 4 and Figure 5, assuming a limit value for the oxygen concentration equal to 17 % and 15 %, respectively. We have chosen these limits because they represent two significant concentrations in the real test in Bonfini et al. (2013): an oxygen concentration of 17 % is the minimum oxygen concentration reached after about 24 min, while an oxygen concentration of 15 % represents a concentration that is never reached. The flow rate of the nitrogen spilled using gas bottles is equal to $0.375 \text{ m}^3 \text{ s}^{-1}$, continuously from the time instant 0 min to the time instant 50 min. A forced ventilation airflow (return air) begins from the time instant 9 min and stops at the 50 min, and its flow rate is equal

to $15 \text{ m}^3 \text{ s}^{-1}$. The volume of the working environment is equal to 24 m^3 . Furthermore, $p_{\text{we}}(0) = p_{\text{oc}}(0) = 101325 \text{ Pa}$. In this case $\delta t = 3 \text{ min}$.

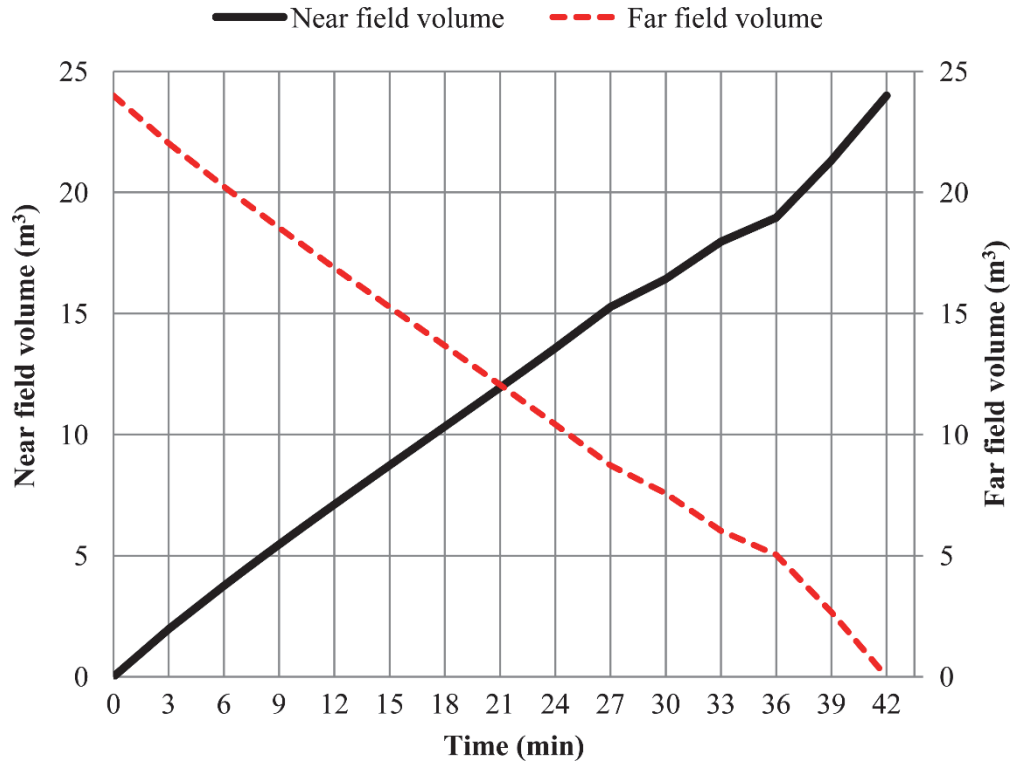


Figure 4: NF and FF volumes in the case study of Bonfini et al. (2013), $C_{\text{O2,NF}}(t) = 17 \%$

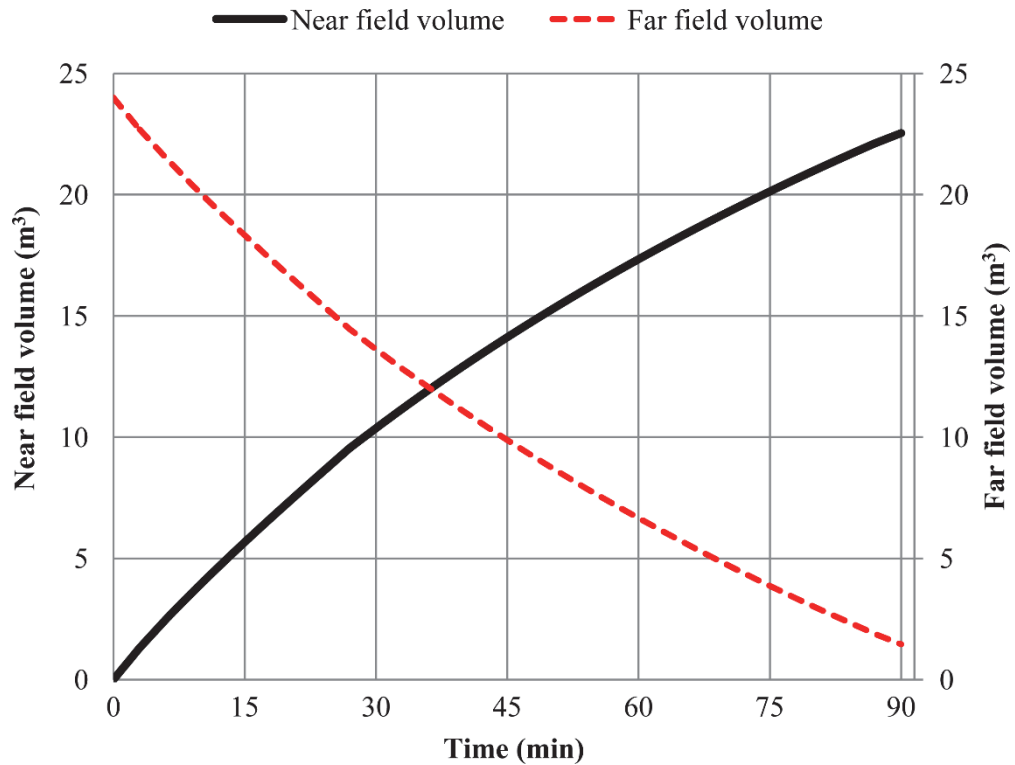


Figure 5: NF and FF volumes in the case study of Bonfini et al. (2013), $C_{\text{O2,NF}}(t) = 15 \%$

When the limit value for the oxygen concentration is equal to 17 % (Figure 4), the NF fills the working environment. This happens after about 42 min. At this instant, no FF exists anymore: the oxygen concentration in the whole working environment is equal to the limit value for the oxygen concentration (i.e. 17 %). This result means that there is the time necessary for organising an orderly evacuation. The radius of the hemisphere is equal, for instance, to 1.70 m at $t = 18 \text{ min}$, and to 1.99 m at $t = 30 \text{ min}$.

The real test in Bonfini et al. (2013) highlights that the sensor detects an oxygen concentration of 17 % after about 24 min. Thus, our NF-FF model is the best performing since it is the closest to the reality: differently from the other models, the NF-FF model reaches the measured value of oxygen concentration, even if with some minutes of delay. Clearly, this delay could be due to the position of the sensor in the real test.

Regarding the case where the limit value for the oxygen concentration is equal to 15 % (Figure 5), the NF does not reach the dimension of the working environment during the entire simulation time of 90 min. This result is in accordance with the one obtained in the real test in Bonfini et al. (2013). At the end of simulation, the distance (i.e. the radius of the hemisphere of the NF) is equal to 2.21 m.

4.3 Case study of Delayen et al. (2001)

The application of the NF-FF model to the case study of Delayen et al. (2001) produces the results pointed out in Figure 6 and Figure 7, assuming the random airspeed at the boundary of the NF equal to 0.06 m s^{-1} and 0.02 m s^{-1} , respectively. The limit value for the oxygen concentration is equal to 17 %. The flow rate of the nitrogen is equal to $0.2 \text{ m}^3 \text{ s}^{-1}$ for 540 s and then stops. The nitrogen release occurs from a container located in a partially enclosed space in Argonne National Laboratory (Illinois), where there is also a ventilation airflow (supply air). In particular, we assumed that its temperature is equal to 293.15 K, its composition to 79 % of nitrogen and 21 % of oxygen, and its reliability to 1. This airflow lasts for 1000 s, and its flow rate is equal to $1.1 \text{ m}^3 \text{ s}^{-1}$. The volume of the working environment is equal to 160 m^3 . In addition, $p_{\text{we}}(0) = p_{\text{oe}}(0) = 98658.27 \text{ Pa}$.

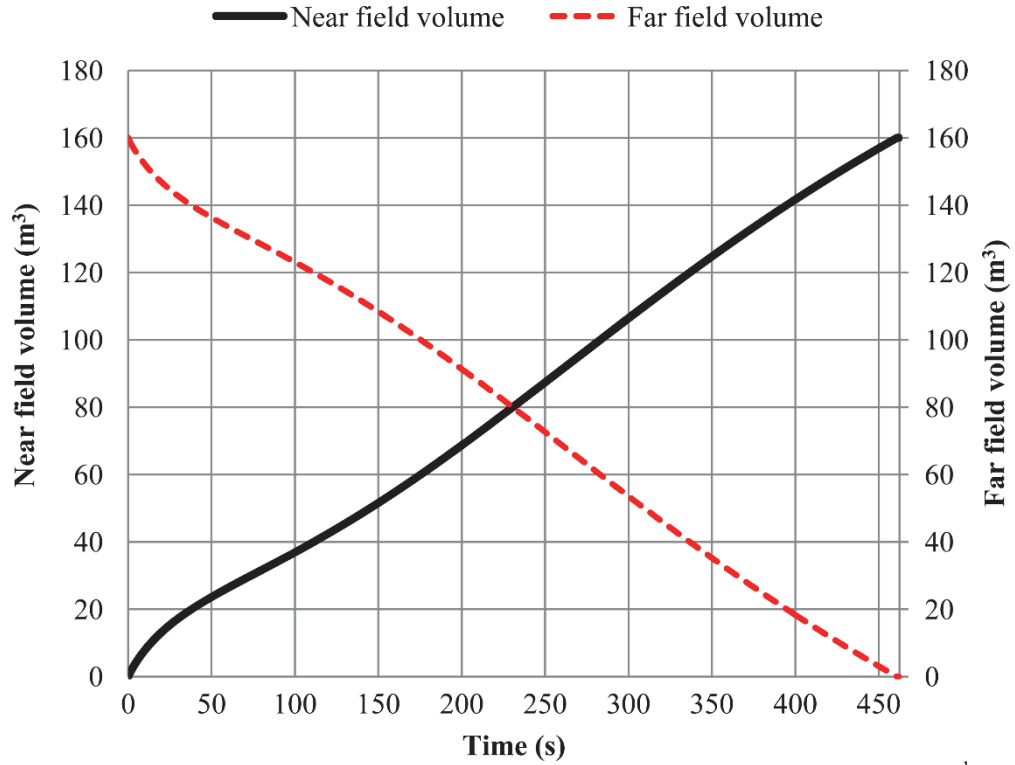


Figure 6: NF and FF volumes in the case study of Delayen et al. (2001), $s = 0.06 \text{ m s}^{-1}$

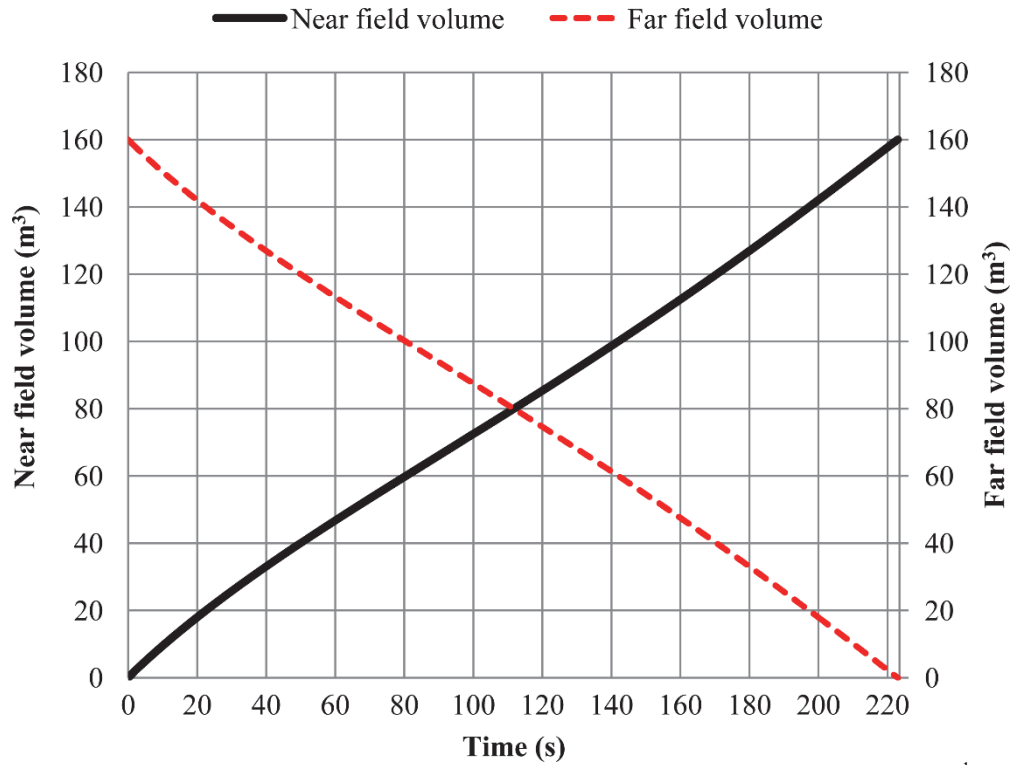


Figure 7: NF and FF volumes in the case study of Delayen et al. (2001), $s = 0.02 \text{ m s}^{-1}$

As depicted in Figure 6 and Figure 7, the NF is equal to the working environment at $t = 462 \text{ s}$ and $t = 223 \text{ s}$, respectively. The parameter s influences the interzonal exchanges: a lower random airspeed at the boundary between the NF and the FF provokes a smaller amount of interzonal exchanges. This phenomenon, comparing these two scenarios and due to ventilation airflows, causes a shorter time for the volume of the NF to become equal to the working environment volume. Because the temporary value of the oxygen concentration (i.e. $\tilde{C}_{O_2, \text{NF}}(t)$) is less than the limit value for the oxygen concentration in all time instants considered in the scenarios, the flow of air (n_{air}) proceeds from the FF to the NF. In particular, in the case of a lower random airspeed (Figure 7), this flow of air, the NF volume and its radius are greater than the values obtained in Figure 6. The radius of the hemisphere representing the NF changes during the simulations: for instance, at the time $t = 50 \text{ s}$ the radius is equal to 2.24 m for $s = 0.06 \text{ m s}^{-1}$, and to 2.67 m for $s = 0.02 \text{ m s}^{-1}$.

In both scenarios, NF fills the entire working environment within few seconds and thus the entire area must be evacuated immediately. Indeed, the limit value of oxygen equal to 17 % can cause decreased ability to perform tasks, increased breathing volume, accelerated heartbeat, and dizziness.

4.4 Case study of Stefana et al. (2016)

Stefana et al. (2016) apply their well-mixed model to the same case studies discussed above. In the following, we propose a comparison among their results and the ones obtained through our NF-FF model. Table 5 points out the values of oxygen concentration in the working environment, and of the time obtained through the well-mixed model (Stefana et al., 2016) and the NF-FF model. The values of oxygen concentration are the outputs obtained by the application of the well-mixed model, and we consider them as inputs for setting the limit value for the oxygen concentration in the NF-FF model. From the point of view of the NF-FF model, time represents the instant when the NF volume becomes equal to the working environment one.

Table 5: Comparison among the results of the well-mixed and the NF-FF models

| Case study | Concentration (%) | Time | |
|-----------------------|-------------------|--------------------------------------------|-------------|
| | | Well-mixed model (Stefana et al., 2016) | NF-FF model |
| Augustynowicz (1993) | 17.02 | 77 s | 73 s |
| | 10 | 272 s | 246 s |
| | 4 | 608 s | 575 s |
| Bonfini et al. (2013) | 19.41 | 15 min | 15 min |
| | 18.67 | 24 min | 24 min |
| | 17 | - | 42 min |
| Delayen et al. (2001) | 19 | 118 s | 96 s |

| | | | |
|--|----|-------|-------|
| | 18 | 321 s | 187 s |
| | 17 | - | 462 s |

With regard to the case study of Augustynowicz (1993), we can note that the application of NF-FF model allows to reach the limit prior to the well-mixed model based on the assumption of perfect mixing within the working environment. This consideration is also valid for the scenarios based on the case study of Delayen et al. (2001). Note that through the well-mixed model an oxygen concentration of 17 % is never reached.

In the case of Bonfini et al. (2013), the well-mixed model never reaches an oxygen concentration of 17 %, while our NF-FF model allows to obtain this concentration after a simulation time of about 42 min. In the other two simulated scenarios the times obtained through the two models are the same. These results can be justified by the assumption of the case study related to the duration of δt , which is equal to 3 min and thus does not allow to realise a detailed simulation.

In summary, we can state that the NF-FF model is more precautionary than the well-mixed one.

5 Discussion

Our NF-FF model is based on the balances of mass of air and moles of oxygen in both NF and FF. Similarly to NF-FF models available in the literature, the NF contains the contaminant sources (in our case: inert gas), while the FF the rest of the working environment (e.g. ventilation airflows). Differently from NF-FF models available in the literature, our model assumes that the NF volume is not a constant value, but it varies over time for assuring a limit value for the oxygen concentration defined and fixed by the risk assessor. The trend of the NF size can be a useful data for the risk assessor in order to determine the safety distance from point source releases, and improve the emergency response plan. Furthermore, this NF-FF model allows to: define customisable indoor and outdoor parameters, consider the existence of both forced and natural ventilation, take into account reliability of storage and/or distribution and of ventilation systems, and analyse voluntary and accidental releases of inert gases, simultaneous substances, or mixtures. In addition, it is able to estimate the volume that contains a limit value for the oxygen concentration and thus to better predict the oxygen level in space, considering the working environment composed by two well-mixed fields.

In general, the risk assessor during the application of such an approach has to take into account some of its limitations, mainly the difficulty in the determination of the interzonal airflow rate and the lack of consideration of the actual existence of a continuous concentration gradient. An important assumption of this new NF-FF model regards its applicability in case of multiple releases only if the set of these releases can be supposed as point. However, this assumption may be unrealistic and/or generate errors in the estimates: in these cases, the definition and application of a zonal model would be appropriate.

The analyses of the case studies available in the literature represent a preliminary step to the phase of actual validation. Our NF-FF predictive model has produced interesting results in these case studies and has provided more realistic estimates of exposures than the ones provided by well-mixed models. The tests have pointed out that the outputs of the model are also consistent with the expected oxygen contents. In particular, a reduction of the limit value for the oxygen concentration leads to an increase of the time required to achieve the equivalence between NF and working environment. Furthermore, the NF-FF model reaches the limit value for the oxygen concentration in the entire working environment in a time of the same order of magnitude as the time in which the well-mixed models obtain the same value of oxygen concentration. Specifically, the NF-FF approach is more precautionary because the time in which the model proposed in this paper attains this limit is below the time obtained by the well-mixed models.

6 Conclusions

This study presents the first model predicting the indoor oxygen level based on a NF-FF approach. For this reason this model allows to assess ODH in any working environment where inert gas releases can occur, in a more accurate way than the well-mixed models available in the literature. This model helps safety managers to take into consideration the spatial variability of the oxygen content in a workplace, regardless the country, the company, and the type of the working environment. Moreover, it is the first model estimating the indoor oxygen level in space (even though partially due to the assumptions of the NF-FF approach) and in time simultaneously.

In particular, this model is able to estimate the NF volume containing a limit value for the oxygen concentration. The risk assessor can apply the model choosing any desired geometry of the NF, and the type (in terms of concentration by volume and/or atmospheric partial pressure) and the value of the oxygen limit that are suitable for the scenario and situation under evaluation.

The implementation of this model allows the risk assessor to identify a critical portion of the volume, varying in time, in which the oxygen concentration is equal to a limit value for the oxygen concentration. Sometimes, its application can also provide information on the safety distance that the operator must keep from the release point to prevent the asphyxiation risk.

In addition, the model outputs can be obtained relatively quickly: it seems a good compromise between a well-mixed model and more complex models. Indeed, a NF-FF model is less precise, but computationally more convenient than CFD models.

Future works may include validating the results obtained in all case studies with CFD modelling, studying new scenarios responsible to ODH, and modelling more than two fields for studying more accurately the variation of oxygen content in a working environment, i.e. using a zonal approach.

Appendix 1

General assumptions

- The only cause of ODH taken into consideration in the model is represented by releases of inert gases. Other potential causes of ODH such as chemical reactions and vaporisation of cryogenic liquids are out of the field of application.
- In our model, mass balances of the substances and mixtures used in the working environment are applied. In particular, our model is based on the balances of mass of air and moles of oxygen in each field. Consequently, the model is characterised by four balances.
- In the working environment there are two types of systems: storage and/or distribution systems of inert gases, and ventilation systems. Storage and/or distribution systems can also be equipped with local exhaust systems to capture gases, vapours, or dusts: the moles of substances and mixtures actually released into the working environment are quantified subtracting from the total released moles those that are extracted from the local exhaust system.
- The ideal gas constant R is equal to $8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$ (IUPAC, 2014).
- We neglect effects of water vapour and humidity.
- Air in the working environment, inert gases released into the volume, airflows introduced into and/or drawn from the working environment are assumed as ideal gases.
- The air and the flows within each field are perfectly mixed, and thus the oxygen content is uniform in each box.
- The NF contains inert gas sources, which are the storage and/or distribution systems of inert gases. The sources of inert gases are thus concentrated in a point of the NF. Furthermore, the NF is centred on the inert gas sources.
- The FF is the volume outside the NF, and includes airflows related to forced (both supply and return) and natural ventilation.
- The NF and the FF volumes are not constant values and can vary over time. In particular, the NF volume can increase or decrease (as well as the FF volume).
- The sum of volumes of the NF and the FF is the overall volume of the working environment.
- Between the two fields there is an interzonal airflow $\beta \text{ (m}^3 \text{ s}^{-1}\text{)}$. This parameter can vary over time, and depends on the volume of the NF in the previous time instant.
- The NF is completely contained in the working environment volume. Note that in the cases in which the NF size exceeds the maximum size allowed in a direction of the working environment, the risk assessor should change the geometry of the NF.
- No net advective flow in the space surrounding the pollutant source is assumed. No advective flow would result in symmetrical concentrations around the source (Keil, 2015).

Assumptions related to indoor parameters

- Some indoor parameters are customisable and settable by the risk assessor, such as the sizes of the working environment volume and thus the indoor air volume, the initial indoor air composition and thus the initial oxygen concentration, the initial indoor air temperature of the working environment.
- The working environment volume remains constant.
- In order to assure the equilibrium between the indoor air pressure and the outdoor pressure, we assume the existence of natural ventilation, infiltration, and/or exfiltration.
- The temperature of the working environment can vary over time due to the mixing of flows with different temperatures. At each instant time, the working environment is characterised by a mixing of flows that leads to a uniform equilibrium temperature. We assume that the temperature of the NF and the one of the FF are the same at each instant.
- The limit value for the oxygen concentration of the NF is customisable, and can be set by the risk assessor in every time instant.
- At each time instant, the pressure of the NF and FF are the same and uniform throughout the working environment.

Assumptions related to outdoor parameters

- Also some outdoor parameters can be chosen by the risk assessor: the air temperature, the air pressure, and the outdoor oxygen concentration. According to ISO (1975), the standard thermodynamic air temperature and the standard air pressure at mean sea level are equal to 288.15 K and to 101325 Pa, respectively.
- The value of the outdoor oxygen concentration may change based on a specific time and on the particular supply air sub-system of ventilation systems.
- The outdoor pressure can vary during the time interval under analysis and in which the model is applied. As a consequence, the indoor pressure changes in order to maintain the equilibrium between inside and outside. A change of the outdoor pressure also affects the volume of the NF.

Assumptions related to ventilation aspects

- In the FF, one or more HVAC-R systems, with supply air and/or return air sub-systems, may be located.
- The air introduced into the working environment (i.e. supply air) by ventilation systems and the air introduced into the working environment in a natural way through the phenomenon of natural ventilation are mixed uniformly, completely, and instantaneously with the air in the FF volume.
- We have considered the air introduced into or drawn from the working environment as the mix of oxygen, some pure inert gases, and some impurities (e.g. water vapour).
- Each airflow provided by supply air sub-systems can be set in terms of flow rate, oxygen concentration, composition, and temperature. Furthermore, we have supposed that the different supply air sub-systems introduce airflows depending on weather conditions.
- Forced ventilation airflow rates (supply air and return air) can be set in time, and the reliability of HVAC-R systems is considered.
- The air drawn from the working environment by return air sub-systems and the air drawn from the working environment in a natural way through the phenomenon of natural ventilation have the composition, and thus the oxygen concentration, of the indoor air of the FF at the instant previous to the one being analysed.
- We have supposed airflows of natural ventilation, infiltration, and exfiltration driven by the pressure difference inside and outside the working environment. In the paper, we indicate as “natural ventilation” the contribution of infiltration, exfiltration, and the proper natural ventilation.

Assumptions related to causes and releases

- The only cause of ODH that we consider is the release of inert gases, which are nitrogen, helium, argon, krypton, xenon, and radon. From the point of view of ODH assessment, we also include carbon dioxide because can cause an asphyxiation effect, as underlined by Han et al. (2014).
- Only one substance and/or mixture, or more substances and/or mixtures simultaneously can be released. Note that the model is applicable in case of multiple releases if the set of these releases can be assumed as point.
- The inert gases released by storage and/or distribution systems can be not pure, and so include some impurities (e.g. solid particles, water vapour, and other gases including oxygen and carbon dioxide). Therefore, we have assumed each inert gas released into the working environment as constituted by the main pure inert gas and some impurities: oxygen, other pure inert gases, and other impurities (i.e. different from oxygen, and other pure inert gases).
- The composition of substances and mixtures released into the working environment can be set in order to discriminate among the main pure inert gas, oxygen, other pure inert gases, and other impurities.
- The releases of inert gases can be voluntary or accidental, as well as instantaneous, finite/temporary, or continuous.
- The flows of released substances and mixtures are mixed uniformly, completely, and instantaneously with the air in the NF.
- The reliability of storage and/or distribution systems is considered. Indeed, a voluntary release occurs when there are no failures that prevent the proper operation modes of the systems.
- The accidental releases can occur due to only one failure or more failures simultaneously. The probability that storage and/or distribution systems fail and cause accidental releases is considered. This probability of releases related to a specific failure is equal to 0 if there are no releases due to this failure, otherwise it is equal to a value between 0 (excluded) and 1.
- Release flow rates are expressed as time-dependent functions.
- Each release is characterised by a proper value of temperature and pressure.

Appendix 2

The equations related to the estimation of $n_{\text{air}}(t-\delta t, t)$ and $n_{\text{NF}}(t)$ are demonstrated as follows.

The difference between $C_{\text{O}_2, \text{NF}}(t)$ and $\tilde{C}_{\text{O}_2, \text{NF}}(t)$ is reported in Eq. (A1).

$$C_{\text{O}_2, \text{NF}}(t) - \tilde{C}_{\text{O}_2, \text{NF}}(t) = \frac{n_{\text{O}_2, \text{NF}}(t)}{n_{\text{NF}}(t)} - \frac{\tilde{n}_{\text{O}_2, \text{NF}}(t)}{\tilde{n}_{\text{NF}}(t)} = \frac{\tilde{n}_{\text{O}_2, \text{NF}}(t) + n_{\text{O}_2, \text{air}}(t-\delta t, t)}{\tilde{n}_{\text{NF}}(t) + n_{\text{air}}(t-\delta t, t)} - \frac{\tilde{n}_{\text{O}_2, \text{NF}}(t)}{\tilde{n}_{\text{NF}}(t)} = \quad (\text{A1})$$

$$\begin{aligned}
&= \frac{\tilde{n}_{NF}(t) [\tilde{n}_{O2,NF}(t) + n_{O2,air}(t-\delta t, t)] - \tilde{n}_{O2,NF}(t) n_{NF}(t)}{\tilde{n}_{NF}(t) n_{NF}(t)} = \frac{\tilde{n}_{NF}(t) \tilde{n}_{O2,NF}(t) + \tilde{n}_{NF}(t) n_{O2,air}(t-\delta t, t) - \tilde{n}_{O2,NF}(t) n_{NF}(t)}{\tilde{n}_{NF}(t) n_{NF}(t)} = \\
&= \frac{\tilde{n}_{NF}(t) \tilde{n}_{O2,NF}(t) + \tilde{n}_{NF}(t) n_{O2,air}(t-\delta t, t) - \tilde{n}_{O2,NF}(t) [\tilde{n}_{NF}(t) + n_{air}(t-\delta t, t)]}{\tilde{n}_{NF}(t) n_{NF}(t)} = \\
&= \frac{\tilde{n}_{NF}(t) \tilde{n}_{O2,NF}(t) + \tilde{n}_{NF}(t) n_{O2,air}(t-\delta t, t) - \tilde{n}_{O2,NF}(t) \tilde{n}_{NF}(t) - \tilde{n}_{O2,NF}(t) n_{air}(t-\delta t, t)}{\tilde{n}_{NF}(t) n_{NF}(t)} = \\
&= \frac{\tilde{n}_{NF}(t) n_{O2,air}(t-\delta t, t) - \tilde{n}_{O2,NF}(t) n_{air}(t-\delta t, t)}{\tilde{n}_{NF}(t) n_{NF}(t)}
\end{aligned}$$

Equations from Eq. (A2) to Eq. (A6) allow to obtain $n_{air}(t-\delta t, t)$ based on adjustments of Eq. (A1).

$$\frac{\tilde{n}_{NF}(t) n_{O2,air}(t-\delta t, t) - \tilde{n}_{O2,NF}(t) n_{air}(t-\delta t, t)}{\tilde{n}_{NF}(t) n_{NF}(t)} = C_{O2,NF}(t) - \tilde{C}_{O2,NF}(t) \quad (A2)$$

$$\tilde{n}_{NF}(t) n_{O2,air}(t-\delta t, t) - \tilde{n}_{O2,NF}(t) n_{air}(t-\delta t, t) = [C_{O2,NF}(t) - \tilde{C}_{O2,NF}(t)] \tilde{n}_{NF}(t) n_{NF}(t) \quad (A3)$$

$$\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) n_{air}(t-\delta t, t) - \tilde{n}_{O2,NF}(t) n_{air}(t-\delta t, t) = [C_{O2,NF}(t) - \tilde{C}_{O2,NF}(t)] \tilde{n}_{NF}(t) n_{NF}(t) \quad (A4)$$

$$n_{air}(t-\delta t, t) [\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t)] = [C_{O2,NF}(t) - \tilde{C}_{O2,NF}(t)] \tilde{n}_{NF}(t) n_{NF}(t) \quad (A5)$$

$$n_{air}(t-\delta t, t) = \frac{[C_{O2,NF}(t) - \tilde{C}_{O2,NF}(t)] \tilde{n}_{NF}(t) n_{NF}(t)}{\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t)} \quad (A6)$$

In Eq. (A6) there is $n_{NF}(t)$ that is unknown. In order to estimate the number of moles in the NF at the instant t , we use the following system of equations:

$$\begin{cases} n_{air}(t-\delta t, t) = \frac{[C_{O2,NF}(t) - \tilde{C}_{O2,NF}(t)] \tilde{n}_{NF}(t) n_{NF}(t)}{\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t)} \\ n_{NF}(t) - n_{air}(t-\delta t, t) = \tilde{n}_{NF}(t) \end{cases}$$

By solving this system of equations (from Eq. (A7) to Eq. (A11)), we obtain $n_{NF}(t)$.

$$n_{NF}(t) - \tilde{n}_{NF}(t) = \frac{[C_{O2,NF}(t) - \tilde{C}_{O2,NF}(t)] \tilde{n}_{NF}(t) n_{NF}(t)}{\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t)} \quad (A7)$$

$$n_{NF}(t) - \tilde{n}_{NF}(t) - \frac{[C_{O2,NF}(t) - \tilde{C}_{O2,NF}(t)] \tilde{n}_{NF}(t) n_{NF}(t)}{\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t)} = 0 \quad (A8)$$

$$\begin{aligned}
&n_{NF}(t) \frac{[\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t)] - \tilde{n}_{NF}(t) [\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t)]}{\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t)} \\
&- \frac{[C_{O2,NF}(t) - \tilde{C}_{O2,NF}(t)] \tilde{n}_{NF}(t) n_{NF}(t)}{\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t)} = 0
\end{aligned} \quad (A9)$$

$$\begin{aligned}
&n_{NF}(t) [\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t) - \tilde{n}_{NF}(t) C_{O2,NF}(t) + \tilde{n}_{NF}(t) \tilde{C}_{O2,NF}(t)] = \\
&= \tilde{n}_{NF}(t) [\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t)]
\end{aligned} \quad (A10)$$

$$n_{NF}(t) = \frac{\tilde{n}_{NF}(t) [\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t)]}{\tilde{n}_{NF}(t) C_{O2,NF,ForFF}(t-\delta t) - \tilde{n}_{O2,NF}(t) - \tilde{n}_{NF}(t) [C_{O2,NF}(t) - \tilde{C}_{O2,NF}(t)]} \quad (A11)$$

References

- Adamowski, M., 2010. CO2 Hazard and ODH. Project CMS Upgrade Cooling System Test Design, Mechanical Department Engineering Note, Particle Physics Division, Fermilab. Number: MD-ENG-250.
- Alicino, M., Ferroni, L., Lazzaro, O., 2008. Valutazione dei rischi connessi con gli usi industriali dell'azoto. Proceedings of Valutazione e Gestione del Rischio negli Insediamenti Civili ed Industriali (VGR), Pisa, Italy (in Italian).
- Amyotte, P., 2013. An introduction to dust explosions: understanding the myths and realities of dust explosions for a safer workplace. Butterworth-Heinemann, Oxford. ISBN: 978-0-12-397007-7.

- Amyotte, P.R., 2014. Some myths and realities about dust explosions. *Process Safety and Environmental Protection*, 92(4), 292-299. DOI: 10.1016/j.psep.2014.02.013.
- Arenius, D., Curry, D., Hutton, A., Mahoney, K., Prior, S., Robertson, H., 2002. Investigation of personal and fixed head oxygen deficiency hazard monitor performance for helium gas. *AIP Conference Proceedings*, 613, 1784-1791. DOI: 10.1063/1.1472217.
- Augustynowicz, S.D., 1993. ODH, Oxygen Deficiency Hazard Cryogenic Analysis. Superconducting Super Collider Laboratory.
- Blyukher, B., 1995. Oxygen Deficiency Hazard (ODH) Analysis for Pressure and Cryogenic Systems Facilities. *Proceedings of the Pressure Vessels and Piping Conference 1995: Structural Integrity of Pressure Vessels, Piping, and Components (PVP)*, 318, 169-176.
- Bonfini, G., Gabriele, F., Tobia, M., Tartaglia, R., Giampaoli, A., 2013. Nitrogen gas spillage in a confined space located in the Gran Sasso Underground Nuclear Physics Laboratory: an outstanding oxygen deficiency hazard case study, in: Garzia, F., Brebbia, C.A., Guarascio, M. (Eds.), *Safety and Security Engineering V*, WIT Transactions on The Built Environment, 134, WIT Press, Southampton, Boston, pp. 145-153. DOI: 10.2495/SAFE130141
- Chorowski, M., Konopka-Cupiał, G., Riddone, G., 2006. Safety oriented analysis of cold helium–air mixture formation and stratification. *Cryogenics*, 46(4), 262-272. DOI: 10.1016/j.cryogenics.2005.11.019.
- Crozier, J.W., 2008. Safety handling procedures for cryogenic materials. Office of Health and Safety, Fulton School of Engineering, Arizona State University.
- Danyluk, Q., Hon, C.Y., 2006. Are Mathematical Models an Appropriate Surrogate for Exposure Monitoring when Establishing Respiratory Protective Requirements for the Clean-up of Small Indoor Chemical Spills? *WorkSafeBC*. WCB File: RS2003/04-DG03. Available on http://www.worksafebc.com/contact_us/research/research_results/res_60_10_230.asp (accessed on March, 2016).
- Delayen, J.R., Schlenker, R.A., Shepard, K.W., Specht, J.R., Young, L., 2001. *Physics Division Cryogenic Safety Manual*. Physics Division Cryogenic Safety Committee. Argonne National Laboratory, Argonne, Illinois.
- Earnest, C.M., Corsi, R.L., 2013. Inhalation exposure to cleaning products: application of a two-zone model. *Journal of Occupational and Environmental Hygiene*, 10(6), 328-335. DOI: 10.1080/15459624.2013.782198.
- Feigley, C.E., Bennett, J.S., Khan, J., Lee, E., 2002. Performance of deterministic workplace exposure assessment models for various contaminant source, air inlet, and exhaust locations. *American Industrial Hygiene Association Journal*, 63(4), 402-412. DOI: 10.1080/15428110208984728.
- Fermilab (Fermi National Accelerator Laboratory), 2009. Oxygen Deficiency Hazards (ODH). FESHM 5064. Fermilab ES&H Manual.
- Fermilab (Fermi National Accelerator Laboratory), 2015. Oxygen Deficiency Hazards (ODH). FESHM 4240. Fermilab ES&H Manual.
- Furtaw Jr., E.J., Pandlan, M.D., Nelson D.R., Behar, J.V., 1996. Modeling indoor air concentrations near emission sources in imperfectly mixed rooms. *Journal of the Air and Waste Management Association*, 46(9), 861-868. DOI: 10.1080/10473289.1996.10467522.
- Gaffney, S., Moody, E., McKinley, M., Knutsen, J., Madl, A., Paustenbach, D., 2008. Worker exposure to methanol vapors during cleaning of semiconductor wafers in a manufacturing setting. *Journal of Occupational and Environmental Hygiene*, 5(5), 313-324. DOI: 10.1080/15459620801988014.
- Han, S.H., Chang, D., Kim, J., Chang, W., 2014. Experimental investigation of the flow characteristics of jettisoning in a CO₂ carrier. *Process Safety and Environmental Protection*, 92(1), 60-69. DOI: 10.1016/j.psep.2013.10.003.
- Hemeon, W.C., 1963. *Plant and Process Ventilation*. Second Edition. Industrial Press, New York. ISBN: 9780831130206.
- Hofstetter, E., Spencer, J.W., Hiteshew, K., Coutu, M., Nealley, M., 2013. Evaluation of recommended REACH exposure modeling tools and near-field, far-field model in assessing occupational exposure to toluene from spray paint. *Annals of Occupational Hygiene*, 57(2), 210-220. DOI: 10.1093/annhyg/mes062.
- Iarocci, M., 1994. Calculation of Oxygen Deficiency Hazard Classes for RHIC. RHIC Project, AD/RHIC/RD-72. Brookhaven National Laboratory.
- ISO (International Organization for Standardization), 1975. ISO 2533, Standard Atmosphere.
- IUPAC (International Union of Pure and Applied Chemistry), 2014. *Compendium of Chemical Terminology*. Gold Book. IUPAC. Version 2.3.3. Durham, North Carolina.
- Jayjock, M., Logan, P., Mader, B., Owens, J., Eldridge, J., Costello, M., Morken, M., Lieder, P., 2011a. Modeled comparisons of health risks posed by fluorinated solvents in a workplace spill scenario. *Annals of Occupational Hygiene*, 55(2), 202-213. DOI: 10.1093/annhyg/meq062.
- Jayjock, M.A., Armstrong, T., Taylor, M., 2011b. The Daubert standard as applied to exposure assessment modeling using the two-zone (NF/FF) model estimation of indoor air breathing zone concentration as an example. *Journal of Occupational and Environmental Hygiene*, 8(11), D114-D122. DOI: 10.1080/15459624.2011.624387.
- Jefferson Lab, 2014. Oxygen Deficiency Hazard. Information book.
- Jia, L.X., Wang, L., 2002. Equations for gas releasing process from pressurized vessels in ODH evaluation. *AIP Conference Proceedings*, 613, 1792-1798. DOI: 10.1063/1.1472218.
- Jones, R.M., Simmons, C., Boelter, F., 2011. Development and evaluation of a semi-empirical two-zone dust exposure model for a dusty construction trade. *Journal of Occupational and Environmental Hygiene*, 8(6), 337-348. DOI: 10.1080/15459624.2011.576330.
- Keil, C., Murphy, R., 2006. An application of exposure modeling in exposure assessments for a university chemistry teaching laboratory. *Journal of Occupational and Environmental Hygiene*, 3(2), 99-106. DOI: 10.1080/15459620500498109.
- Keil, C.B., 2000. A tiered approach to deterministic models for indoor air exposures. *Applied Occupational and Environmental Hygiene*, 15(1), 145-151. DOI: 10.1080/104732200301962.
- Keil, C.B., 2015. Experimental measurements of near-source exposure modeling parameters. *Journal of Occupational and Environmental Hygiene*, 12(10), 692-698. DOI: 10.1080/15459624.2015.1029619.
- Keil, C.B., Simmons, C.E., Anthony, T.R., 2009. *Mathematical Models for Estimating Occupational Exposure to Chemicals*. American Industrial Hygiene Association, Fairfax, VA 22031. ISBN: 978-1-935082-10-1.
- Lopez, R., Lacey, S.E., Jones, R.M., 2015. Application of a Two-Zone Model to Estimate Medical Laser-Generated Particulate Matter Exposures. *Journal of Occupational and Environmental Hygiene*, 12(5), 309-313. DOI: 10.1080/15459624.2014.989361.
- Luke, J., 2004. *Liquid Nitrogen - Storage, Use and Transportation Within College Premises*. Guidance Note 015. Safety Department, Imperial College London, London.
- Miller, T.M., & Mazur, P.O., 1984. Oxygen Deficiency Hazards Associated with Liquefied Gas Systems: Derivation of a Program of Controls. *American Industrial Hygiene Association Journal*, 45(5), 293-298. DOI: 10.1080/15298668491399811.
- Morgan, S., 2014. *Working with Cryogenic Gases*. OSHEU Guidance. Cardiff University.
- Nicas, M., 1996. Estimating exposure intensity in an imperfectly mixed room. *American Industrial Hygiene Association Journal*, 57(6), 542-550. DOI: 10.1080/15428119691014756.

- Nicas, M., 2016. The near field/far field model with constant application of chemical mass and exponentially decreasing emission of the mass applied. *Journal of Occupational and Environmental Hygiene*, 13(7), 519-528. DOI: 10.1080/15459624.2016.1148268.
- Nicas, M., Armstrong, T.W., 2003a. Computer implementation of mathematical exposure modeling. *Applied Occupational and Environmental Hygiene*, 18(8), 566-571. DOI: 10.1080/10473220301417.
- Nicas, M., Armstrong, T.W., 2003b. Using a spreadsheet to compute contaminant exposure concentrations given a variable emission rate. *American Industrial Hygiene Association Journal*, 64(3), 368-375. DOI: 10.1080/15428110308984829.
- Nicas, M., Neuhaus, J., 2008. Predicting benzene vapor concentrations with a near field/far field model. *Journal of Occupational and Environmental Hygiene*, 5(9), 599-608. DOI: 10.1080/15459620802282375.
- Nicas, M., Plisko, M.J., Spencer, J.W., 2006. Estimating benzene exposure at a solvent parts washer. *Journal of Occupational and Environmental Hygiene*, 3(5), 284-291. DOI: 10.1080/15459620600637390.
- Persoons, R., Maitre, A., Bicout, D.J., 2011. Modelling the time profiles of organic solvent concentrations for occupational exposure assessment purposes. *Annals of Occupational Hygiene*, 55(4), 421-435. DOI: 10.1093/annhyg/meq090.
- Ramachandran, G., 2005. *Occupational Exposure Assessment for Air Contaminants*. CRC Press, Boca Raton ISBN: 978-1-5667-0609-4.
- Sahmel, J., Unice, K., Scott, P., Cowan, D., Paustenbach, D., 2009. The use of multizone models to estimate an airborne chemical contaminant decay profile: occupational exposures of hairdressers to vinyl chloride in hairspray during the 1960s and 1970s. *Risk Analysis*, 29(12), 1699-1725. DOI: 10.1111/j.1539-6924.2009.01311.x.
- Sakhvidi, M.J.Z., Barkhordari, A., Salehi, M., Behdad, S., Fallahzadeh, H., 2013. Application of mathematical models in combination with Monte Carlo simulation for prediction of Isoflurane concentration in an operation room theater. *Industrial Health*, 51(5), 545-551. DOI: 10.2486/indhealth.2012-0130.
- SLAC (Stanford Linear Accelerator Center), 2015. *Cryogenic and Oxygen Deficiency Hazard Safety*. Chapter 36, ESH Manual.
- Spencer, J.W., Plisko, M.J., 2007. A comparison study using a mathematical model and actual exposure monitoring for estimating solvent exposures during the disassembly of metal parts. *Journal of Occupational and Environmental Hygiene*, 4(4), 253-259. DOI: 10.1080/15459620701205253.
- Stefana, E., Marciano, F., Alberti, M., 2016. A predictive model for estimating the indoor oxygen level and assessing Oxygen Deficiency Hazard (ODH). *Journal of Loss Prevention in the Process Industries*, 39, 152-172. DOI: 10.1016/j.jlp.2015.11.022.
- Stefana, E., Marciano, F., Cocca, P., Alberti, M., 2015. Predictive models to assess Oxygen Deficiency Hazard (ODH): a systematic review. *Safety Science*, 75, 1-14. DOI: 10.1016/j.ssci.2015.01.008.
- Vadali, M., Ramachandran, G., Mulhausen, J., 2009. Exposure modeling in occupational hygiene decision making. *Journal of Occupational and Environmental Hygiene*, 6(6), 353-362. DOI: 10.1080/15459620902855161.