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TOXIC EFFECTS IN AN INDUSTRIAL AREA

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Abstract

In this paper emission distribution in the atmosphere was considered. Pollutants in combination may show antagonistic, reduced, additive, sum of individual pollutant effects, or synergistic, additive effects. Pollutant concentration effects depend on pollutants concentration thresholds. Hazard estimation refers to threshold parameter. Aero-pollutant transfer modeling involves diffusion, mixing an force fields driving. Effect of environmental turbulence was considered. In this paper toxic emissions distribution in an industrial area was examined.

Key words: Air pollutant; transport; model; multipolutant; diffusion.

1. Introduction

Pollutant gas such as sulfur dioxide and nitrogen oxides are frequently emitted in combination normally with other pollutants such as soot and heavy metal particles, in many places, of the plants to one of them may photooxidants are emitted simultaneously ^[1-3]. In these cases, the effects of combination of pollutants are not simply the sum of the effects of individual components, but the relative concentration of components or the specific sensitivity of the plants to one of them may determine to response. Thus, pollutant in combination may display antagonistic, reduced, additive, sum of individual pollutant effects, or synergistic, superadditive effects.

Gaseous deflagrations in equipment in industry at pressures higher than ambient atmosphere give rise to extremely severe explosion consequences for property and life. Explosion relief venting method is a commonly used method in avoiding this loss. The method can vent the explosion to the outside space, generally the ambient air, through a device of low pressure resistance opening when the explosion is in development and the overpressure exceeds a certain safe threshold ^[4-7].

During venting, the unburned flammable mixture is ejected firstly from the vent opening to form an external combustible cloud, and it is ignited by the subsequent vented flame to result in an external explosion. This presents potential explosion damage to neighboring structure or equipment or personal in the vicinity. Therefore, it is necessary to investigate the pressure and flow structure characteristics of the external flow field in venting.

A series of tests in different venting conditions were performed in a large scale explosion chamber ^[7]. The experimental results showed the external explosion generated by the released gas ignited by the jet flame and its influence on the internal overpressure.

In order to practical application, many empirical and semi-empirical calculation methods for venting were widely used, but the great majority was only applied to the internal flow field ^[8-10]. A data correlation to calculate the external pressure, based on the spherically symmetric blast wave model and ellipsoidal blast wave model, were suggested. But this calculation method did not incorporate the effects of and the interaction of turbulence and flame in the external flow field were yet not well understood owing to the complexity or vented explosion. The characteristics of the intensity of secondary explosion were discussed in detail under different conditions, such as failure pressure, ignition location, vent area and equivalence ratio of the gas mixture. Obvious changes of the dynamic structure of the external flow field during

venting would occur due to the coupling of the internal and external flow field when the membrane ruptured. Therefore, there existed a low pressure area, a high pressure area and a leading shock wave in turn far from the opening in the external flow field during venting. The variation characteristics of intensity of the external secondary explosion under different venting conditions were noted in the pressure time history.

Even people obey regulation, accidents have occurred. In this paper toxic effects of aeropollutants combination were considered..

2. Pollutant combination effects

Global heating and air pollution are occupied engineers which treating »green house effects« reduction. Huge emissions fluorids, carbon dioxid, sulphur dioxid, etc. have decreased ozone in atmosphere.

In the past, most experiments on exposure to combinations of pollutants were carried out under laboratory conditions using higher concentrations of gases than are typical in the field. Newer fumigation techniques, for instance open top chambers or field fumigation systems, have now enabled the exposure of plants under field conditions with increasingly realistic concentration ranges. These experiments indicate that pollutant combination effects depend on pollutant concentration SO_2 and O_2 are often antagonistic at levels where the individual gases cause severe leaf injury, while superadditive effects predominate at lower concentrations ($SO_2 < 140 \mu g/m^3$, $O_2 < 100 \mu g/m^3$), particularly near the threshold dosage. In addition the injury symptoms for SO_2 and O_2 in combination are not a simple mixture, frequently, the symptoms of one pollutant occur more clearly than those of the other ^[5].

With regard to combination SO_2 , NO_2 , and O_2 , effects were produced in many plants by lower concentrations of NO_2 , and the other gases than if they acted alone, especially at the lower exposure levels. Synergistic effects of NO_2 in combination with SO_2 or O_2 apparently results from a decrease of the nitrate and nitrite reductase activities. While the latter tend to rise in response to NO_2 , acting on its own, activation of these reducing enzymes is limited or even suppressed by the simultaneous with SO_2 or O_2 .

This adverse effect is further enhanced by the formation of free radicals. An inhibitory influence on the regulation of transpiration occurred at less than $20.10^{-6} \text{dm}^3/\text{m}^3 SO_2 + 20.10^{-6} \text{dm}^3/\text{m}^3 NO_2$. The combination NO_2 with O_2 is likely to endanger vegetation more than $NO_2 + SO_2$ in combination and should receive greater attention since these pollutants form essential components of photochemical smog. The treat to vegetation may increase still further if all three pollutants interact simultaneously.

Combination effects, however, also depend n the temporal order in which the pollutions affect the plants. If they are first exposed to NO_2 and thereafter to SO_2 , the usual SO_2 effects are reduced, while the opposite sequences causes superadditive effects because SO_2 affects nitrite reductase. Attention must also be drawn to the combination of gaseous SO_2 with acid precipitation, the effects of this combination are discussed in connection with the new types of forest damage.

In conclusion, and with some reservations resulting from above remarks, critical levels for short term and long term exposure may be defined. In view of the fact that must horticultural and agricultural plants do not show adverse effects at sulphur dioxide concentrations $SO_2 < 20 \ \mu g/m^3$, while particularly sensitive species of trees, moss, lichens, and bushy and grassland vegetation are adversely influenced by concentrations of $\sim 20 \ \mu g/m^3$, the critical level for acting on its own is to be set at $20 \mu g/m^3$ ($\sim 0.007 \text{cm}^3/\text{m}^3$) as the annual mean value. Experimental fumigation trials that indicate first adverse effects from 70 $\mu g/m^3$ SO₂ (~ 0.025 ppm) for cultivated plants form the basis for setting the short term value this concentration.

The toxic effects thresholds determination are in general conservative, thus helping the establishment operators and local authorities to effectively protect people. At the same time, the overestimation of effects puts more pressure on and may impose severe limitations on the future development of establishment.

Still, there is no common definition of methodology and thresholds of concern of physical effects to the environment. Each state defined its own methodology and thresholds through which they systematically define the extent of the areas affected by different physical consequences.

Oxidizing substances in contact with combustible substances, give off oxygen or other oxidizing agents so as or increase the danger of fire or the vigor with which the combustibles burn. As a rate, oxidizing substances are not themselves combustible. Various mixtures of the test substance with cellulose powder are prepared and the burning rate of a reference mixture of barium nitrate and cellulose. A substance is classified as oxidizing if the burning rate of a test mixture is greater than that of the reference mixture. As a rule, incorrect predictions are made if this test procedure is applied to liquids or to melting and highly flammable, combustible, substances, so its use with these substances is ruled out. A comparable test methods is employed internationally for transportation of hazardous substances. In some instances, the two procedures give different classifications or the same substance.

Oxidizing properties make a chemical a hazardous substance, and safety regulations apply to its storage and transportation.

3. Emissions distribution

A long range transport of air pollutions has largely been limited to species. Firstly, the inorganic nitrates representing nitric acid, HNO3, and aerosol nitrate, to contribute to the acidification problem.

The aircraft designer must minimize the structural weight, subject to the structure having sufficient strength and stiffness to carry the critical design loads safety. The cruising altitude should be chosen so as to minimize fuel consumption.

Advanced aero-pollutant transfer modeling involves diffusion, mixing and force fields driving. This category of problems can be treated alternatively by concept of material, energy and momentum transport. These models are derived in microscopic and macroscopic levels for material, moment and energy transport ^[8].

Pollutants are spreading in atmosphere by free and limited. If consideration is isolated local zone then space variables and time can be introduced in description. When wind occurs effects of viscosity dispersion can be neglected in the equations. Wind influences dependent of flow direction and model is derived in wind blowing direction. Wind velocity is defined through geometrical velocities.

In the case boundary likes mountings chosen zone must be divided into subzones and then summary effects to be considered. In this case before modeling need to take geographical mapping.

The frequency function of a population is completely determined once its parameters are known. For example, the binomial distribution is completely determined by the parameters n, the number of independent trials and p, the probability of success in a single trial. An important problem in statistics is to estimate the population parameters, given a random sample drawn from the population. If the form of the frequency function is assumed, then values for its parameters may be determined by forming the likelihood function, which gives probability that the given sample came from a population with the assumed frequency function. The likelihood function is thus a function of the unknown parameters. The values of the parameters are now estimated by maximizing the likelihood function with respect to these parameters, subject to any constraints that may be present. The resulting optimal values of the parameters are known as maximum likelihood estimates. The method may be applied to functions of discrete of continuous variables.

In the cases when several factors influence to success trial, no aiding, but attribute with their quantities logarithm normal distribution can be applied. For example, problems particle dimension, condensation, aerosols, petrochemistry, emission etc.

4. Toxic emission moving in the atmosphere

The motion of a small particle placed in an environmental fluid is influenced by the turbulence and accordingly is random. When the motion processes randomness, it is accompanied by diffusion. The diffusion due to the turbulence of environmental fluids is called "turbulent diffusion" in order to distinguish it from the molecular diffusion associated with the random molecular motion that constitutes heat.

The theory of the variation of diffusion width of a group of particles takes the standard deviation of the particle distribution as the "diffusion width", in the case of diffusion from an instantaneous source, the time a continuous source, the variation of spread as a function of

distance from the source is considered. From a this standpoint, scientists deal with the square of the standard deviation, i.e. the statistical variance σ^2 , rather than the standard deviation itself.

In this toxic emission transport, multidimensional model on different micro- and macrolevels was considered. The model gives flow description in atmosphere and can used for atmospheric conditions prediction.

Aero-pollutants concentrations and temperatures fields in industrial zone need to predict. For arbitrary considered region contours conditions should be state before started the partial differential equations solving.

$$\frac{\partial \psi_c}{\partial t} + v_x \frac{\partial \psi_c}{\partial x} = D(\frac{\partial^2 \psi_c}{\partial y^2} + \frac{\partial^2 \psi_c}{\partial z^2})$$

where v geometrical velocity, ψ_c is particle distribution probability concentration function, *D* is diffusivity, and *t* is time.

The derived mathematical model can be used for aero-pollutants concentration and temperatures field prediction. The finite difference numerical method for the partial differential equations solution was used.

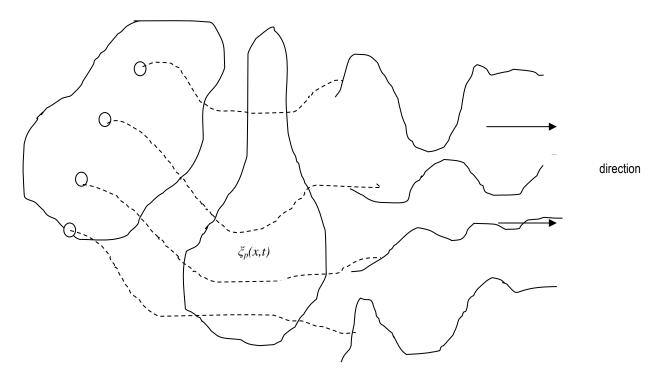


Fig.1 Toxic substance moving

If a stochastic quantity *X* has normal distribution then and *ln X* distributed according to normal probability low. At the pollutants expansion in atmosphere free and forced moving are happened.

There are three spatial independent variables and time: x,y,z and t. As dependent variables can be considered aero-pollutants concentrations. Effects of gravity wind, raining, hail and the others can be take into account. Let consider entity distribution in space, $\psi_X(x, y, z, t, \xi_1, \xi_2, ..., \xi_m)$ and for arbitrary selected spatial region: Such as there are 3+m independent variables plus time, which can be developed as 3+m dimension space material transport for considered entity. For arbitrary small space local zone is obtained:

For solving equations of the derived model need to define initial and boundary condition. By derived mathematical model simulation procedure can be provided for various situations.

The obtained model can be used for emissions concentration prediction over towns. Also, temperature fields spreading can be simulated. The obtained results can be used for impact

(1)

analysis conditions to pollutants transfer and their emission in atmosphere without external forces.

By simulation experiments is carrying out analysis of the parameters values which obtaining during the process simulation, that is similarity with physical experiments. Advantage is, that simulation enabling virtual system representation and difference in results depends only from controlled input parameters. Requested modifications follow results analysis, it gives iterative character in achievement new knowledge about system.

5. Smog and acid rain

Gaseous combustion products contribution in various ways to the greenhouse effect and acid rain, and can produce a direct health hazard due to the formation of smog (Fig.2).

In the process requires a furnace or steam boiler to provide hot utility then any excessive use of hot utility will produce excessive utility waste. Improved heat recovery will reduce the overall demand for utilities and hence reduce utility waste.

For example, this reduction in utility demand resulted in the following reduction in emissions from power stations on the site.

The choice of fuel for furnaces and steam boilers affects both the amount and composition of gaseous utility waste. For example, a switch from coal to natural gas in a steam boiler can cut carbon dioxide emissions by typical 40% for the same heat released. This result from the lower carbon content of the natural gas. In addition, it is likely that the switch from coal to natural gas will also considerably reduce both SO_x and NO_x emissions [10].

Such a fuel switch, whist being desirable in reducing emissions, might well be expensive. If the problem is SO_x and NO_x emissions there are other ways to combat these.

There are four ways to reduce SO_x emissions. On the principle that is better not create waste in the first place, rather than create it and then treat it, SO_x emission reduction should be tackled in the following order:

- *Increase the energy efficiency of the process*. This decreases the amount of fuel burnt and hence decreases *SO_x* emissions at source.
- *Switch to a low sulphur fuel*. This is an and obvious solution but may expensive.
- *Desuphurize the fuel*. Most types of fuel can be desulphurized, but this becomes increasingly difficult as goes from gaseous to liquid to solid fuels.
- Desuphurize the fuel gas. A whole range more than one of processes have the been developed to remove *SO_x* from fuel gases: injection of limestone into the furnace, absorption into wet limestone after the furnace, absorption into aqueous potassium sulphite after the furnace and many others ^[19].

However, the by products from many of these desulphurisation processes cause major disposal problems.

In dealing with NO_x that there are two main reaction paths for NO_x formation thermal home and NO_x from fuel bound nitrogen.

Thermal NO_x forms, particularly at high temperatures, by the reactions:

 $N_2 + O_2 \Leftrightarrow 2NO$

(Fuel N)+1/2 $O_2 \Leftrightarrow NO$

 $NO + 1/2O_2 \Leftrightarrow NO_2$

 $NO + 1/2O_2 \Leftrightarrow NO_2$

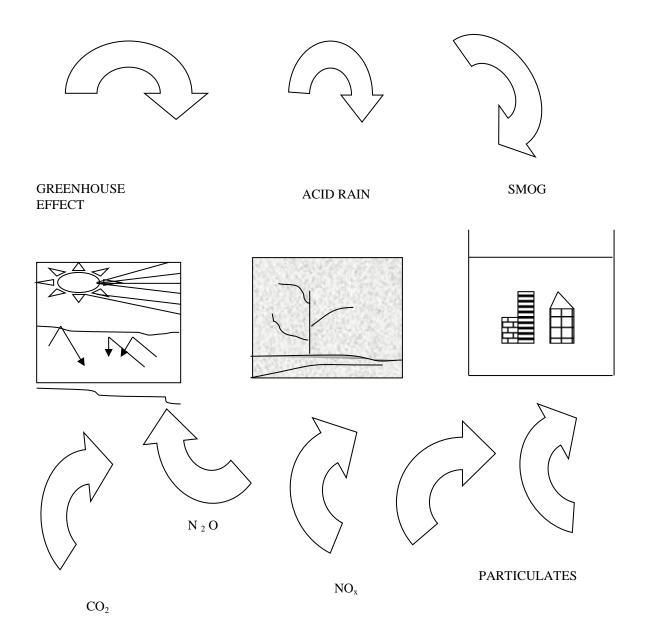
Fuel bound NO_x forms at low as well as high temperatures. However, part of the fuel-bound nitrogen reacts directly to N_2 and N_2O and N_2O_4 are also formed in various reactions, all of which adds to the complexity of NO_x formation. It is virtually impossible to calculate a precise value for the NO_x emitted by a real device.

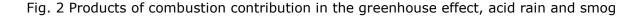
Emissions depend not only on the type of combustion technology but also its size and the type of fuel used. There are five ways to reduce NO_x emissions:

- Increase energy efficiency. As with NO_x emissions, the less fuel burns produce less NO_x.
- *Switch fuel. NO_x* formation is fuel dependent, and the general trend is that moving from solid to liquid to gaseous fuel decreases the amount of *NO_x*. However, let emphasize again that this is also very much dependent on the combustion device.

- Low *NO_x* burners or staged combustion. Low *NO_x* burners reduces *NO_x* formation by inducing fuel-air mixing patterns which lead to lower peak flame temperatures. Injection of the fuel in stages, injection of the air in stages or steam injection are possible. *NO_x* reductions of the order of 50-70% are possible by changing the burner design.
- *Fuel gas recirculation*. Recirculating part of the flue gas towers the peak flame temperature, thus reducing thermal NO_x formulation. There is clearly a limit to how much flue gas can be recirculated without affecting the stability of the flame. NO_x reductions of the order of 40% are possible.
- Chemical reduction. The injection of ammonium cuts NO_x emissions by reducing NO_x to nitrogen and water. Although it can be used at higher temperatures without a catalyst, the most commonly used method injects the ammonium into the flue gas upstream of a catalyst bed, typically vanadium and/or tin on silica support. These techniques can be used in isolation or in combustion.

SO_x





The sensitivity analysis techniques are applied to several modules. This case study concentrates on to carbon dioxide cycle module. The dike raising modules are described. One consequences of higher sea level is the need to rise the dike's height. A survey of the greenhouse effects for society many articles are considered.

In the greenhouse model all factors are quantitative, but the techniques also apply to qualitative factors. The sensitivity analysis techniques are applied. A simulation model maps its inputs into one or more outputs, hence a simulation model is a mathematical function. Mathematical models explain the input/output behavior of the underlying simulation model.

One of the major imminent ecological threats of the world is the enhanced greenhouse problem, the earth and the lower layers of its atmosphere have shown rising temperatures over the past hundred years. This phenomenon is probably caused by an increase of greenhouse gases such as carbon dioxide, methane and ozone, that absorb the earth heat radiation so the global average temperature rises. Mankind is largely responsible for this increased greenhouse gas concentration. Temperature are expected to rise further, but with different amounts in different regions of the earth. Higher temperature will cause thermal expansion of the oceans and melting of arctic ice, which raise the sea level. Many models of carbon dioxide cycle can be proposed, one for the oceans and one for terrestrial biosphere ^[9].

Traditionally, industries have not been models of good communication with society, indeed, secretiveness and confidentially were deeply entrenched in the cultures of many reputable companies. Starting with the disclosure of financial information, however, enterprises have increasingly adopted a more open attitude. A similar evaluation has occurred in the environmental domain.

Furnaces, steam boilers, gas turbine and diesel engines all produce gaseous waste as product of combustion. The principal offenders here are oxides of sulphur and nitrogen, particulates, metal oxides, unburnt carbon and hydrocarbons, and of increasing concern, carbon dioxide.

Coal combustion also produces solid waste –ash while steam systems produce aqueous waste from boiler feedwater treatment, boiler blowdown and lost condensate. The recirculating cooling water systems used on most chemical processes also create aqueous waste through cooling tower blow down.

The streams created by utility systems tend to be less environmentally harmful than process waste, but this is no reason for complacency.

6. Conclusion

In this paper toxic effects in industrial zone were examined. Emissions distribution and their interactions were considered. The aero- pollution distribution models were developed and toxic emission moving in the atmosphere were examined. Oxidizing substances in combustion area were considered.

The obtained distributed model can be used for emissions concentration prediction over towns. The model gives flow description in atmosphere and can used for atmospheric condition prediction.

Notation

Greek symbols

C concentration, g/m³

 ψ_c particle distribution function

- D diffusivity, m²/s
- v geometrical velocity

Reference

- [1] Mintz K.J., Bray , M.J. Zuiliany, D.J.Amyotte, P.R., Pegg, M.J.: Inerting of fine metallic powders, Journal of Loss Prevention, in the Process Industries, vol.9, 1996, p.77-80.
- [2] Amyotte, P.R, Pegg, M.J.,Khan,F.I.:Application of inherent safety principles to dust explosion prevention and mitigation, *Process safety and Environment Protection*, vol.87,2009,35-39.
- [3] Savković-StevanovićJ., R.Pjanovic, N.Boskovic-Vragolovic:Chemicals and Hazard, EED11-WSEAS, 9th International Conference on Environment, Ecosystems and Development,ID669-267, Monteruex, Switzerland, 29-31 December, 2011.

- [4] Savković-StevanovićJ.: Simulation aided process safety, IES2009 Proceedings-19th Symposium and Seminar on Information and Expert Systems in the Process Industries,pp.83,Belgrade, 30-31 October,2009, ISBN978-86-911011-3-8.
- [5] Vanderstraeten, B., Tuerlinckx, D., Berghmans , J., Vliegen, S., Oost, E.V., and Smit, B.: Experimental study of the pressure and temperature dependence, *J. Hazard. Mater.*, vol.56, no.3, 1997, p.237-246.
- [6] Mosorinac, T., Stevanovic-Huffman, M.M., Savkovic-Stevanovic, J.:Chemical process plant toxic effects, *Procedia Engineering*, 2012, Science Direct, Elsevier, www.elsevier.com /bcate/ procedia, www.sciencedirect.com.
- [7] Savkovic-Stevanovic J.:Safety of the chemical processes, p. 489-584, in the Book -Process plant operation, equipment, reliability and control,Eds.Michael Holloway, Chikezie Nwaoha,, and Oliver Onyewuenyi, 768 pages, John Wiley & Sons,New York, ISBN 978-1-1180-2264-1,2012.
- [8] Savković-Stevanović J., L.Zivkovic: Advanced aero-pollutions transfer modelling, CHISA2010-Inter.Congress of Chem. Eng. and Process Engineering, Prague, August 29-Sept.2, 2010.
- [9] Žerajić S.,Savković-Stevanović J.: CO₂ mission control in the atmosphere,IES2013-Proceedings of the Symposium and Seminar on Information and Expert Systems in the Process Industries, pp.188-196, 28-29. oktobar, 2013, ISBN978-86-911011-8-3.
- [10] Savković-Stevanović J.: Global pollution control, IES2013-Proceedings of the Symposium and Seminar on Information and Expert Systems in the Process Industries, pp.197-204, 28-29. Oktober, 2013, ISBN978-86-911011-8-3.