Environment Protection Engineering

Vol. 11 1985 No. 2

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PROBLEMS DEALT WITH IN THE DEODORIZATION OF WASTE GASES

Offensive odours constitute a specific group of substances emitted to the atmosphere in a mixture of various waste gases. The logarithmic relationship between the intensity of odour sensation and the concentration of the odoriferous substance may be explained in terms of the Weber–Fechner law. Thus, to achieve a high degree of deodorization, it is necessary that specialized high-efficiency methods be involved. In this paper, an account of deodorizing methods is included, which might be of utility in solving the complex problem of environmental nuisance due to odour emissions.

With increasing standards of living, annoyance reaction due to exposure to malodorous atmospheric pollutants has become a problem of increasing importance to environmental health. This statement is justified in so far as most of the pollutants emitted to the atmospheric air may be classified as odour-carrying substances.

It is a well-known and established fact that every malodorous pollutant has its specific minimal concentration sensed by the olfactory organ and defined as odour or olfactory threshold. For many malodorous air pollutants, the odour threshold exceeds the maximum allowable concentration (MAC) established in the form of standards with regard to the level of toxicity. Thus, if appropriate measures are taken in order that the MAC values would not be exceeded, we can anticipate that the environment is sufficiently well protected against the undesirable impact of this group of malodorous pollutants.

Analysis of exemplary data included in tab. 1 shows that there exists another group of air pollutants which is relatively numerous and differs from the one mentioned above. This dif-

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ference occurs in the concentrations sensed by smell which are lower than the actual MAC of the pollutants in the atmospheric air. Even at small concentration levels, this group of air pollutants may cause a considerable nuisance to the environment (to say nothing of the toxic influence they may exert when their concentrations exceed the maximum allowable values).

Table 1

Odour thresholds and Polish air quality standards for selected malodorous pollutants

Progi zapachowe i polskie normy jakości powietrza dla wybranych cuchnących zanieczyszczeń

Pollutant	Odour threshold	MAC for protected areas – Single exposure – 30-min averaging time	MAC for protected areas – Single exposure – 24-h averaging time
	mg/m^3 stp		
Ammonia	26×10^{-3}	4×10^{-1}	2×10^{-1}
Dimethyl sulphide	51×10^{-3}	5×10^{-3}	21×10^{-4}
Pyridine	4×10^{-2}	2×10^{-2}	1×10^{-2}
Methyl mercaptan	22×10^{-4}	1×10^{-3}	43×10^{-5}
Valeric acid	26×10^{-4}	3×10^{-2}	13×10^{-3}
Butyric acid	1×10^{-3}	2×10^{-2}	85×10^{-4}
Diethyl sulphide	92×10^{-5}	1×10^{-2}	43×10^{-4}
Hydrogen sulphide	15×10^{-4}	6×10^{-2}	2×10^{-2}
Allyl disulphide	6×10^{-4}	5×10^{-4}	21×10^{-5}
Propyl mercaptan	23×10^{-5}	1×10^{-3}	43×10^{-5}
Ethyl mercaptan	4×10^{-5}	2×10^{-3}	85×10^{-5}
Skatole	4×10^{-7}	1×10^{-3}	43×10^{-5}

According to the definition of the World Health Organization health is a state of good physical, mental and social comfort and not only the absence of diseases or infirmity. In the light of this definition, malodorous pollutants should also be eliminated effectively from the atmospheric air, even though their influence on the environment is detectable through subjective annoyance reactions only.

Odours owe their origin to various sources such as industrial plants (e.g. pulp mills, petroleum refineries, flax and hemp retteries, chipboards manufacturing plants), feedlots, highways or urban agglomerations with heavy traffic. Most of the odour-carrying substances are released to the atmosphere as constituents of waste gases. To comply with the prescribed sanitary standards, it is necessary that the deodorization process be efficient. This can be achieved by a careful selection of deodorizing technologies and installations. Unfortunately, many of those attempts met with little success, because insufficient consideration (if at all) was given to the specific nature of the odoriferous substances to be treated.

Although the olfactory faculty varies from one human being to another, each rise above the odour threshold value is associated with a nonlinear increase in the intensity of the olfactory sensation. It is, however, difficult to quantify this because of the lack of instrumented determination of the olfactory sensation perceived. The difficulty may be partly overcome by making use of what is known as the Weber–Fechner law [1]. The law involves the assumption that the accuracy of estimating perceptions may be determined by the value of perceivable difference. And this means that the parameters describing variable phenomena will not be distinguishable until the variation of those parameters perceivable to our senses exceeds certain values.

Thus if x stands for the intensity of the stimulus expressed in any conventional way (in case of malodorous airborne pollutants it can be, for example, concentration) and Δx is the value of the least perceivable difference, then in accordance with Weber's postulate

$$\frac{\Delta x}{x} = \text{const.} \tag{1}$$

If relationship (1) is true for the least-perceivable difference, it is also true for other values of the rise in stimulus intensity which Fechner expressed as follows:

$$dS = k\frac{dx}{x} \tag{2}$$

where:

dS – intensity rise of sensation due to stimulus intensity rise by dx,
dx – value of stimulus intensity rise,
x – original value of stimulus intensity,
k – factor of proportionality.

After transforming, we obtain the general Weber–Fechner formula:

$$S = a \log x - a \log x_0 \tag{3}$$

where:

S – sensory impression intensity,
x – intensity of stimulus producing impression of S-intensity,
x_0 – intensity of stimulus producing the smallest (liminal) impression,
a – constant.

Making use of the general form of Weber-Fechner´s formula (3), we can accept for the problem of odours intensity that

$$S = \log c - b \tag{4}$$

where:

S – odour sensation intensity,
c – concentration of malodorous pollutants in the air inhaled,
b – constant coefficient of malodorous pollutants under examination.

Relationship (4) is shown graphically in fig. 1.

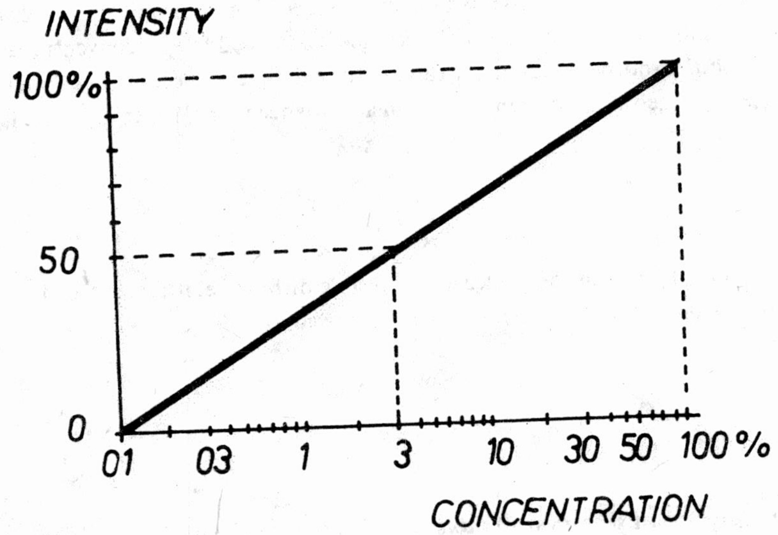

Figure. Relationship between odour intensity and concentration of odour-forming pollutants
Rysunek. Zależność między intensywnością zapachu a stężeniem wywołujących go zanieczyszczeń

It should be emphasized that the relationship under discussion is of particular importance to the deodorization of waste gases. Hence, taking into account the logarithmic character of this relationship, it is obvious that a 50% drop in concentration of malodorous pollutants obtained during deodorization accounts for a poor 10% drop in the intensity of the sensation perceived initially. To make odour intensity decrease by a half, stimulus concentration should be reduced by over 90%. It is interesting to note that an odourless atmosphere will not be obtained until the concentration of malodorous pollutants drops below the odour threshold. This means level as low as a fraction of per cent of the content contributing to the maximal intensity of the perceived sensation. Unfortunately, industrial-scale installations for the treatment of various waste gases usually involve conventional chemisorption methods [2], so they fail to yield the abatement desired.

It is a well-known fact that chemisorption may be efficient for a certain type of pollutants only. Thus, chemisorptive methods account not so much for a full deodorization of the waste-gases under treatment as for eliminating some of the constituents. These being so, it is advisable to apply more versatile methods that will enable the neutralization of all the pollutants included, or at least the removal of odour-producing substances.

Gas adsorption on activated carbon proved to be promising in a number of instances. As activated carbon is a hydrophobic agent, it preferentially adsorbs hydrophobic compounds. In general, activated carbon is considered a useful means of air deodorization for concentrations of pollutants below 5×10^{-4} vol. °/o [3]. It should, however, be noted that the adsorbent of interest is used on the replacement basis. This means that it is discarded when saturated, and replaced by a fresh or regenerated charge. The regeneration procedure involves either hot air or steam. In other words, gas adsorption on activated carbon becomes increasingly uneconomical as the concentration of pollutants in the air to be treated and, consequently, the frequency of discards tend to increase. All these clearly outline the applications of the method. An interesting effort in this respect is the use of activated-carbon adsorption for deodorizing the ambient air in restaurants, canteens, laundries, etc., rather than in (or around) industrial plants. However, adsorption on activated carbon has the disadvantage that the adsorbent does not fully destroy, but only stores the retained pollutants. A complete destruction of offensive smell is essential as it makes for the efficiency of the deodorization process.

Thermal combustion (flame combustion) proved to be a versatile and destructive method for the degradation of a number of pollutants [4]. Efforts have also been made to apply combustion for the removal of odour-carrying gases [5]. The process involves gas-fired (rather than electrically heated) refractory chambers and requires temperatures of 1000 to 1200 K, depending on the concentration of pollutants. Some of the heat evolved in the course of the reaction may be recuperated in heat exchangers. Apart from this inherent advantage, thermal combustion has the limitation of being a high-cost process which, in addition, requires special safety measures. Many of the gaseous pollutants to be treated are flammable, thus creating serious explosion hazards.

Conducted at optimum parameters, thermal combustion is able to yield an almost complete oxidation of air pollutants. Nevertheless, its applicability varies considerably with the composition of the flue gas to be treated. Thus, thermal combustion will successfully destroy hydrocarbons to yield water vapour and acrbon dioxide, which is essential to air pollution control. But the combustion process becomes expensive to maintain when the waste gas mixture includes mercaptans, amines, pyridine compounds, etc., to yield oxygen compounds with heteroatoms (e.g. sulphur dioxide). In all those instances where combustion cannot successfully cope with the type of pollutants, additional treatment is required.

The same comments hold for catalytic combustion. It is interest to mention that some recent efforts are directed at the development of selective catalysts which influence the reaction to yield safe products (i.e., creating no environmental hazards). An interesting example worth mentioning is the transformation process for the removal of mercaptans. In this reaction, mercaptans containing S^{-2} are catalytically converted to elemental sulphur S^{o}.

It should be added that the deodorization methods presented in this short account have some inherent disadvantages. Thus, combustion methods are not cheap to operate because of the high energy demand, adsorption processes involve large amounts of adsorbing material, and chemisorption accounts for considerable environmental nuisance by producing objectionable wastewater. On the other hand, promising attempts are reported from a number of countries, in which much emphasis has been laid on the possible utilization of microorganisms for neutralizing airborne odour-carrying substances.

The use of bacteria for the purpose of deodorization is amongst relatively recent approaches [6], although biological methods (activated sludge process, trickling filter) have been successfully applied for over a hundred years to the treatment of industrial wastewater or municipal sewage. During biological treatment harmful components of the waste gas mixture are oxidized or converted in the presence of microbiological growths. These occur either in the sorptive solution or are immobilized on the bed surface. Owing to the variety of strains, as well as to their great ease of adaptation to various environmental conditions, microorganisms can be applied for the neutralization of various gas mixtures containing both organic and inorganic compounds [7]. Yet, the basic requirements for a successful biodegradation with which the substance to be treated must comply, are the following:

sufficient volatility (molecular weight up to 350),
hydrophilic or lipophilic character,
presence of functional group.

Malodorous pollutants have similar features. It is known, however, that only sufficiently volatile hydrophilic substances have the capacity of reaching olfactoreceptors, the cell membranes of which have a lipidic character and are surrounded by a mucus layer. In this context malodorous pollutants seem to be highly biodegradable. Currently this view is prefered in the literature, and references to successful applications of biological methods are becoming increasingly frequent. Thus, BOHN [8], [9], DRATWA [10]–[12] and HELMER [13], [14] describe examples of deodorization on biofilters which involved soil, compost or specially enriched bacterial cultures. GUST, GROCHOWSKI and SCHIRZ [15] report on the operation of about 50 biofilters of differents size, which have been installed in the Federal Republic of Germany. These filters deodorize gases produced by industrial-scale composting of rubbish and carcass, by animal-waste recovery plants and rooms for multi-herd swine breeding. The description of a large installation including a biological scrubber is found in the papers by KOHLER and PAUL [16] and REITHER [17]. The system works in the ferrous foundry of the Daimler-Benz Works in Untertürkheim. About 10^5 m^3 of gases flow through this installation during one hour. The pollutants to be degraded are the following: malodorous tertiary amines, formaldehyde and phenol. After a few years of work the operating costs of the biological method were found to be as low as one seventh those of chemisorption in $KMnO_4$ solution.

Attempts at deodorizing industrial waste gases in the activated sludge process are also reported [18]. Thus, KOHLER, LACHENMAYER and HOMANS [19] successfully used activated sludge to deodorize waste gases from chipboard manufacture.

Some of the investigations at the Institute of Environment Protection Engineering, Technical University of Wrocław, have progressed along similar lines for two years now. One of our Research Teams is attempting to neutralize, by biological methods, the emissions of formaldehyde and related substances generated during formation of chipboards [20]. This study will have been completed in the nearest future. Another attempt will be directed towards the application of biological methods to the deodorization of the phenol and formaldehyde containing waste gas mixture produced during the manufacture of mineral insulating materials.

REFERENCES

[1] McGAMBLE E. A., Am. J. Psychol., **10**, 82 (1898).

[2] RUTKOWSKI J. D., *Dezodoryzacja gazów odlotowych,* Papers of the Institute of Environment Protection Engineering, Technical University of Wrocław, No. 3, ser. Monogr. No. 8 (1975).

[3] TURK A., *Odor Control,* Kirk-Othner Encyclopedia of Chemical Technology, Vol. 14, ed. by Willey, 1967.

[4] KOHL A. L., RIESENFELD F. C., *Oczyszczanie gazów,* WNT, Warszawa 1965.

[5] SAWATANI T., *Problems of Obnoxious Odor in Industrial Pollutions,* preprint, 17-th Seminar, Assoc. Safety Eng., Yokohama 1970.

[6] POMEROY R. D., *De-odoring of Gas Streams by the Use of Microbiological Growths,* U.S. Patent 2,793,096 (1957).

[7] JAGER J., SCHILDKNECHT H., Staub-Reinh. Luft, **5**, 145 (1979).

[8] BOHN H. L., J. Environ. Qual., **1**, 372 (1972).

[9] BOHN H. L., Compost Science, **17**, 15 (1976).

[10] DRATWA H., Deutsche Geflügelwirtsch., **15**, 276 (1967).

[11] DRATWA H., Schweinezucht und Schweinemast, **15**, 147 (1967).

[12] DRATWA H., Staub-Reinh. Luft, **28**, 516 (1968).

[13] HELMER R., Ges.-Ing., **95**, 21 (1974).

[14] HELMER R., Müll und Abfall, **5**, 140 (1974).

[15] GUST M., GROCHOWSKI H., SCHIRZ S., Staub-Reinh. Luft, **11**, 397 (1979).

[16] KOHLER H., PAUL E., Staub-Reinh. Luft, **38**, 15 (1978).

[17] REITHER K., TL – Umweltschutztechnik, **30**, 5 (1977).

[18] KOHLER H., HOMANS W. J., BARDTKE D., GWF – Wasser/Abwasser, **120**, 282 (1979).

[19] KOHLER H., LACHENMAYER U., HOMANS W. J., Staub-Reinh. Luft, **3**, 102 (1981).

[20] RUTKOWSKI J. D., SZKLARCZYK M., ŚWIETLIK J., CZYSZCZOŃ Z., KĘDZIERSKI L., GOMÓŁKA E., Reports of the Institute of Environment Protection Engineering, Technical University of Wrocław, ser. SPR-68/I-15/84 (1984).

PROBLEMY DOTYCZĄCE ODWADNIANIA SPALIN

Przykre zapachy stanowią specyficzną grupę substancji emitowanych do atmosfery w mieszaninie różnych spalin. Zależność logarytmiczna intensywności wrażenia zapachowego od stężenia substancji zapachowych może być wytłumaczona zgodnie z prawem Webera-Wechnera. Dlatego też, aby osiągnąć wysoki stopień odwonienia, konieczne jest zastosowanie specjalnych metod o dużej skuteczności. W pracy zawarto zestawienie tych metod odwonienia, które mogą mieć zastosowanie w rozwiązywaniu kompleksowego problemu degradacji środowiska w wyniku emisji nieprzyjemnych zapachów.

FRAGEN ZUR GERUCHSLOSMACHUNG

Geruchsstoffe bilden eine spezifische Gruppe von Substanzen, die mit verschiedenen Abgasen in die Atmosphäre gelangen. Die Analyse des sogenannten Weber-Fechnerschen Gesetzes, d.h. der logarithmischen Abhängigkeit der Wahrnehmungsintensität von der Konzentration des Geruchsstoffes, führt zu der Feststellung, dass eine effektive Geruchslosmachung ein hochleistungsfähiges Reinigungsverfahren verlangt. Mit Rücksicht auf diese Eigenart, werden die mit Erfolg angewandten Geruchslosmachungsmethoden beschrieben.

ПРОБЛЕМЫ, КАСАЮЩИЕСЯ ОТХОДЯЩИХ ГАЗОВ

Неприятные запахи составляют специфическую группу веществ, испускаемых в атмосферу в смеси разных отходящих газов. Логарифмическую зависимость интенсивности ощущения запаха от концентрации душистых веществ можно объяснить по закону Вебера-Вехнера. Поэтому, для достижения высокого уровня дезодорации, необходимо применение специальных методов, отличающихся большой эффективностью. В работе имеется сопоставление тех методов дезодорации, которые могут найти применение в решении комплексной проблемы деградации среды в результате эмиссии неприятных запахов.