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Quantitative Estimation of the Emission of Harmful Substances in an Accident at a Chemically Hazardous Site

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Abstract. A methodological approach has been developed to quantify the amount emission harmful substances in an industrial accident. An algorithm for calculating the most probable, acceptable, safe for the environment the amount of harmful substance contained in the release in the event of an emergency at the facility. Adoption of an expedient solution is facilitated by an integrated approach based on determining the parameters of the operation of emergency ventilation and environmental protection measures. The prediction of the amount of harmful substances in the case of mass emissions at a chemically hazardous facility is based on determining the ratio of the height of emission sources, taking into account the differentiation of cleaning methods and their effectiveness.

1. Introduction

As a result of an accident at a chemically hazardous enterprise, it is possible to achieve air quality assurance if technical means and methods of protecting the environment are provided when predicting the most probable amount of harmful substance in the vent.

2. Dynamics of emergency ventilation processes

When calculating the parameters of the purification device, it is expedient to differentiate the purification methods based on the determination of the area of rational purification taking into account the subsequent dissipation of the harmful substance in the environment. Probably possible intervals for changing the amount of harmful substance emissions in case of emergency situations at chemical enterprises, M_i, kg, are considered on the basis of statistical data. In the field of rational cleaning of emissions there must be cleaning devices with a given efficiency and limited overall dimensions under the baseline conditions: with a small excess of the amount of harmful substance emitted relative to the maximum permissible value, the discharge pipe should be installed on the roof of the building, the efficiency factor of the cleaning should be increased; with a significant increase in the amount of harmful substance emitted relative to the maximum permissible value, the discharge pipe should be installed remote, the efficiency factor of the cleaning should be increased; with a significant increase in the amount of harmful substance emitted relative to the maximum permissible value, the discharge pipe must be installed remote, the cleaning efficiency factor has a constant limit value.

Figure 1 shows the dynamics of the concentration of harmful substance in emergency situations, where I, II - the periods of emergency ventilation, the points «A», «B» and «C» indicate the moments of the accident, when the concentration of fire hazardous and explosive harmful substance reaches the

predicted level. Increasing, it takes the maximum value and, as a result of the operation of emergency ventilation, decreases to the maximum permissible value in the working area of the room.
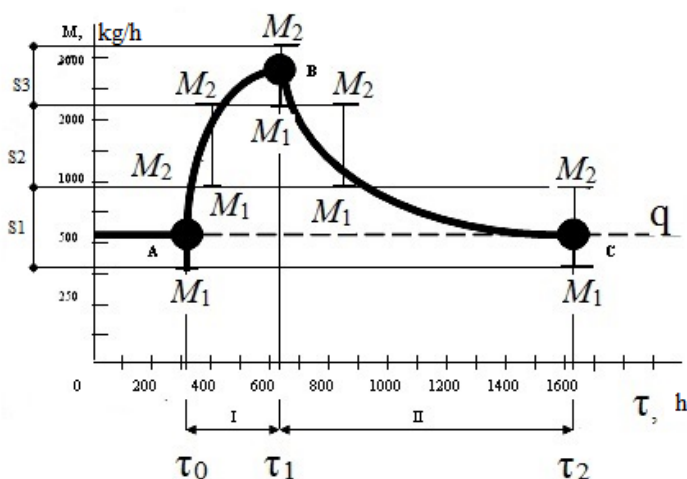

Figure 1. Change in concentration, q, mg/m^3, fire hazardous and explosive harmful substances during an accident and the effect of emergency ventilation: where S1 is the area characterized by the constancy of the concentration in the accidental emission within the limits of permissible values; S2 – area characterized by the content (concentration) of the harmful substance, significantly exceeding the permissible limits; S3 – area characterized by the concentration of harmful substance at the time of the beginning of the accident and the moment of its liquidation; τ_0 – time of the beginning of the accident, hour; τ_1 – time of emergency ventilation, hour; τ_2 – time during which, after the emergency ventilation has been switched on, the concentration of the harmful substance is reduced to the maximum permissible values, h.

3. Quantitative assessment of the emission of harmful substances

The probability of occurrence of an emergency situation is investigated under the conditions listed above. As a result, the most probable scenario of the development of the emergency is determined for the given object, taking into account the amount of harmful substance by means of the dependence:

$$P_A = \frac{M'_A}{M} \tag{1}$$

where M'_A – the most likely amount of harmful substance in the event of an emergency situation with different versions of the accident, kg; M – the maximum possible amount of emission of a hazardous substance in the event of an emergency, kg.

The most likely amount of harmful substance at point "B" is determined by the formula:

$$M'_B \in M_1; M_2 \tag{2}$$

where M_1 – the most likely release of a harmful substance from the area of the minimum excess of its amount in emissions, leading to the need to install the pipe on the roof of the building, kg; M_2 – the most likely release of a harmful substance from the area of maximum increase in its number of emissions, leading to the need to install a remote pipe, kg.

The algorithm for calculating the amount of harmful substance in the volume of the room for the period of time from 0 до τ_1, hour, removed by the emergency ventilation systems transferred for purification and subsequent dispersion in the atmosphere, is presented in the form of a block diagram in Figure 2.
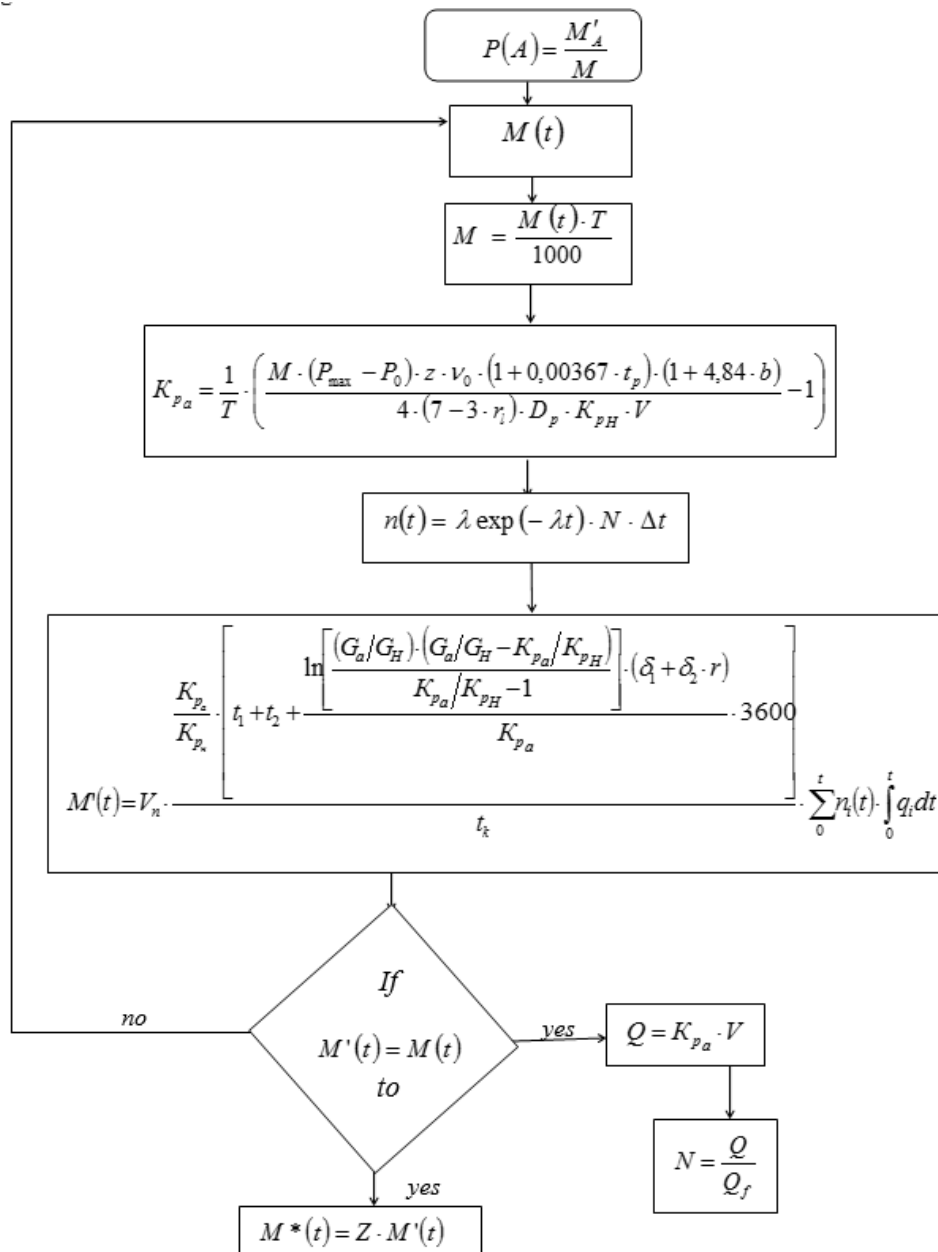
$$P(A) = \frac{M'_A}{M}$$

$$M(t)$$

$$M = \frac{M(t) \cdot T}{1000}$$

$$K_{p_a} = \frac{1}{T} \cdot \left(\frac{M \cdot (P_{max} - P_0) \cdot z \cdot v_0 \cdot (1 + 0{,}00367 \cdot t_p) \cdot (1 + 4{,}84 \cdot b)}{4 \cdot (7 - 3 \cdot r_i) \cdot D_p \cdot K_{pH} \cdot V} - 1 \right)$$

$$n(t) = \lambda \exp(-\lambda t) \cdot N \cdot \Delta t$$

$$M'(t) = V_n \cdot \frac{\dfrac{K_{p_a}}{K_{p_n}} \cdot \left[t_1 + t_2 + \dfrac{\ln\left[\dfrac{(G_a/G_H) \cdot (G_a/G_H - K_{p_a}/K_{pH})}{K_{p_a}/K_{pH} - 1} \right] \cdot (\delta_1 + \delta_2 \cdot r)}{K_{p_a}} \right] \cdot 3600}{t_k} \cdot \sum_0^t n_i(t) \cdot \int_0^t q_i dt$$

If

$$M'(t) = M(t)$$

to

no →

yes → $Q = K_{p_a} \cdot V$

$$N = \frac{Q}{Q_f}$$

yes → $M^*(t) = Z \cdot M'(t)$

Figure 2. The algorithm for calculating the amount of explosives in the emissions of ventilation systems of industrial enterprises in the atmosphere in an emergency situation: $M(t)$ – amount of harmful substance in the volume of the room for a period of time from 0 до τ_1, kg; M – resulted mass of the harmful substance which has arrived in a premise as a result of failure, kg; T – duration of entry of harmful substance into the volume of the room, h; P_{max} – maximum explosion pressure of a stoichiometric gas-air mixture in a closed volume, kPa [1…4]; P_0 – initial pressure, kPa; z – coefficient of participation of the combustible in the explosion; v_0 – molar volume, m³/kmol; t_p – calculated temperature, ℃; 0,00367; 4,84; 4; 7 и 3 – calculated coefficients [5]; b – coefficient that is a function of temperature; D_p – estimated overpressure of the explosion in the room, which determines the category of the room according to the explosion and fire hazard, from [5]; r – coefficient of leakage of the layer blocking the movement of harmful substance from the area of emergency emission localization to the rest of the room; K_{pH} и K_{pa} – multiplicity of air exchange during the operation of the ventilation system under normal technological conditions and in the event of an

accident, respectively, 1/h; V – volume of the room, m^3; $n(t)$ – number of devices (nodes) that failed for a period of time from $t - \frac{\Delta t}{2}$ to $t + \frac{\Delta t}{2}$; Δt – considered time interval, h; t – length of time determined from the interval $t - \frac{\Delta t}{2}$ before $t + \frac{\Delta t}{2}$ to determine the number of failures of apparatuses (nodes) located in a given room volume, h; λ – failure rate; N – number of the same type of apparatus operating in the technological cycle; G_a, G_H – specific release of harmful substance under normal technological conditions and in case of accident, respectively, mg/(m^3·h); δ_1 – the proportion of the volume of the room, corresponding to its part, within which it is necessary to localize the accidental release of the substance; δ_2 – proportion of the volume of the room, corresponding to its part outside the zone of localization of the accidental release of the substance; $q_i(t)$ – concentration of harmful substance in emergency emission, mg/m^3; t_k – calendar time of work of equipment, h; Q – required air flow, generated by emergency ventilation, m^3/h; Q_f – capacity of the fan, m^3/h [6 ... 11]; Z – fraction of the mass of vapor-gas substances participating in the explosion [12...22]; M^* – mass of gas-vapor substances emitted into the atmosphere in the event of an emergency at an industrial facility, kg.

The sequence of quantitative evaluation of the quantity the emission of harmful substances in an accident at a chemically hazardous facility consists of the following main groups: determination of the amount of harmful substance in the discharge of the ventilation systems of the facility in the event of an emergency; determination of the multiplicity of air exchange created by emergency ventilation; specification of the amount of harmful substance in the venting of ventilation systems in the event of an emergency; study of scenarios for the development of the emission of harmful substances and the finding of the most probable current, namely: if the value of M'_A is equal to the value of the total amount of harmful substance in the volume of the room during the period from 0 до τ_1, then it is necessary to determine the required number of fans, N_v or if the value M'_A and the value of the total amount of harmful substance in the volume of the room for a period of time from 0 до τ_1 is not equal, then it is necessary to specify the frequency of air exchange during operation of emergency ventilation, K_{Pa}, 1/h.

The stated calculation technique allows to solve with sufficient accuracy the problem of determining the probable amount of harmful substance in the discharge by ventilation systems of an industrial facility in the event of an emergency situation.

In general, the calculation of the mass of harmful substance emitted by ventilation systems in the event of an emergency situation at a chemically hazardous object is presented in the form of a mathematical relationship:

$$M^* \ t \ = \frac{K_{p_a}}{K_{p_{_H}}} \cdot Z \cdot V \cdot \sum_0^t n_i \ \ t \ \cdot \int_0^t q_i dt \cdot \frac{t_1 + t_2 + t_3}{t_k} \tag{3}$$

where t_1 – time required to turn on emergency ventilation, which is defined as the time spent on detection, the decisions taken and the actual start of the emergency ventilation, h; t_2 – time required for repair, damaged (failed) unit of the device, h; t_3 – the time at which the concentration of the substance will be reduced to a non-hazardous level by means of emergency ventilation, after the source of the emergency supply of the substance has been eliminated, h.

Based on the results of the calculation, the ventilation equipment is selected.

4. Conclusion

The developed algorithm allows to carry out a quantitative assessment of the emission of harmful substances in the event of an accident at a chemical hazardous facility. It is possible to make an assumption about possible ways to achieve the maximum permissible value of the surface concentration of harmful substances in the atmosphere. The quantitative assessment of pollutant emissions allows to predict and reduce the admissible risk and the resulting damage in case of

accidents, taking into account the choice of the most effective technical means [23] and methods of environmental protection.

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