



INVESTIGATION INTO EFFICIENCY OF ADSORPTION PROCESS DURING UTILIZATION OF CURING GASES IN TYRE PRODUCTION

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Received 3 Sept 2005; accepted 23 Nov 2005

Abstract. The problem considered in the paper is mathematical and physical modeling of the adsorption process during utilization of gas emissions of cured tyres and tyre components. The paper contains synthesis and analysis of mathematical models for violent and moderate gassing. It describes an adsorption scheme, formulates an experimental dependence of productivity upon the concentration of emissions in an absorber chamber of a system used for trapping of curing gas emissions and vapors.

Keywords: tyre, curing gases, volatile combinations, utilization, adsorption process.

1. Introduction

Curing equipment for tyres is one of the sources that evolve very intensively harmful gas agents to the ambient production area. Mixed with the vent emissions these gases come to the environment.

At a curing temperature of 153÷180 C° and the productivity of brand special purpose equipment of 30÷2500 kg/h, the amount of released gases is 15÷1700 g/h, accordingly. Curing gases contain up to 400 different components, including 12 carcinogenic nitrosamines.

2. Problem statement

At present there are several methods for trapping and neutralization of curing gases. The most promising one is an absorption method [1-2] in combination with adsorption and micro filtration by membrane filters. However, the fact that there is no mathematical description of the gas emission process taking place by mold opening and tyre unloading prevents development and implementation of adsorption methods into production.

3. Investigation methodology

We use the classical theses of heat and mass transfer

theory as a study tool. In this work the following conventional and simplifying assumptions are used [3-4]:

- Close to the surface of a gassing source all the parameters of vapor and gas mixture are taken as in equilibrium, and in the chamber itself they are not in equilibrium (due to the fact that resistance of both phases influences considerably the character of the mass transfer process).
- A set of liquid components contained in the system is an ideal mixture, i.e. it obeys the Raoult law.
- Equilibrium values of partial vapor pressures in the immediate proximity of a treated surface are set instantly in accordance with temperature change in a liquid phase.
- Flows of gases and vapors through a material surface are equal at all the points of the surface.
- Heat released in the process of material treatment is spent completely on the increase of gas and vapor mixture temperature in the chamber.
- Gas and vapor mixture components released during tyre curing obey the ideal gas laws.
- We understand flows of a partial component as independent, since it was earlier accepted that a combination of liquid components was an ideal

mixture. Other assumptions will be introduced further, if necessary. Designation of literal notations and symbols standing for physical and chemical characteristics and technological parameters is given in the paper in a traditional form [5].

4. Mathematical modeling of processes taking place with gas emissions of small quantities

To evaluate the temperature of a gas and vapor mixture we formulate an equation of heat balance:

$$\begin{aligned} \rho_{mix} C_{mix} V_{mix} \cdot dT = \\ \alpha_T (T - T_l) S_{CB} \cdot d\tau - I_{2\Sigma} \rho_{mix} C_{mix} T \cdot d\tau + \\ C_{mix} S_{mix} T \left[\sum_{j=1}^m I_{\Gamma 1j} + \sum_{i=1}^n I_{\Pi li} \right] \cdot d\tau. \end{aligned} \quad (1)$$

The left part of equation (1) reflects the resulting change in heat contents of the gas and vapor mixture, the first member in the right part of the equation is the heat inlet due to heat interchange with the source of the gas emitting surface, the second member is the heat outlet with the outgas mixture, the third member is the heat inlet with the escaped vapors.

Density ρ_{mix} and modular heat capacity of the mixture C_{mix} can be found according to the additivity rule, using Mendeleev – Clapeyron equation:

$$\rho_{cm} = \left(\sum_{i=1}^m M_{\Pi i} P_{\Pi i} + \sum_{j=1}^n M_{\Gamma j} C_{\Gamma j} \right) / RT; \quad (2)$$

$$C_{cm} = \left(\sum_{i=1}^m M_{\Pi i} P_{\Pi i} + \sum_{j=1}^n M_{\Gamma j} P_{\Gamma j} \right) / \left(\sum_{i=1}^m P_{\Pi i} + \sum_{j=1}^n P_{\Gamma j} \right). \quad (3)$$

For a liquid and solid phase, depending on the type of a technological process, heat balance equation will look as follows:

$$\begin{aligned} \rho_l C_l V_l \cdot dT_l = q_p \cdot d\tau + \alpha_T (T - T_l) S_{CB} \cdot d\tau - \\ C_{mix} S_{CB} \left[\sum_{i=1}^m I_{\Pi li} + \sum_{j=1}^n I_{\Gamma 1j} \right] T \cdot d\tau - \\ S_{CB} \cdot d\tau \sum_{i=1}^m I_{\Pi li} \Delta H_{Vi}. \end{aligned} \quad (4)$$

The density and heat capacity of a liquid phase can be found by the following formulas:

$$\rho_l = \sum_{i=1}^m X_i \rho_{li}; \quad C_l = \sum_{i=1}^m X_i C_{li}. \quad (5)$$

For a solid phase, the notation is similar.

The left part of equation (4) reflects the change of heat contents in a liquid or solid phase, the first member

in the right part of the equation characterizes the air inlet as a result of a chemical reaction, the second member describes the heat outlet due to heat interchange with a gas and vapor mixture, the third member is the heat outlet for the escaped gas and vapor mixture, the last component is the heat consumption for vaporization.

In equations (1–5) we use values for heat of liquid vaporization and for heat capacities of liquid, solid and gas components. To calculate these values the following equations can be derived:

- thus vaporization heat of pure substance is defined analytically as the solution of the following equation:

$$\frac{d(\ln P_{VP})}{d(1/T)} = - \frac{\Delta H_V}{R \Delta Z_V}; \quad (6)$$

- value ΔZ_V at a normal boiling temperature can be defined by the formula:

$$\Delta Z_V = \left[1 - 1 / (P_C T_{BG})^3 \right]^{0.5}. \quad (7)$$

Having inserted form (7) into (6) and having evaluated the value ΔH_V as it is, we can deduce a design formula for calculation of ΔH_{VB} at a normal boiling temperature:

$$\Delta H_{VB} = \left[\frac{2,3RT_B T_C K_V \lg P_C}{T_C - T_B} \right] \cdot \left[1 - \frac{T_C^3}{P_C T_B^3} \right]^{0.5}, \quad (8)$$

where K_V is an empirical constant, depending on the temperature:

$$K_V = \begin{cases} 1,04 & \text{at } 200 \text{ } ^\circ\text{K} \leq T_B \leq 300 \text{ } ^\circ\text{K} \\ 1,045 & \text{at } T_B \geq 300 \text{ } ^\circ\text{K} \end{cases}.$$

For calculation of temperature dependence on heat vaporization, it is acceptable to use the Wattson correlation:

$$\Delta H_{V2} = \Delta H_{V1} \left[\frac{1 - T_{\Gamma 2}}{1 - T_{\Gamma 1}} \right]^{0.38}. \quad (9)$$

Insertion of (8) into (9), under condition that $\Delta H_{V1} = \Delta H_{VB}$, $\Delta H_{V2} = \Delta H_V$, leads to the equation

$$\begin{aligned} \Delta H_V = \left[\frac{2,3RT_B T_C K_V \lg P_C}{T_C - T_B} \right] \times \\ \left[1 - \frac{T_C^3}{P_C T_B^3} \right]^{0.5} \cdot \left[\frac{1 - T_{\Gamma 2}}{1 - T_{U1}} \right]^{0.38}. \end{aligned} \quad (10)$$

In such a way it is possible to calculate vaporization heat of the first i component at an arbitrary temperature.

To calculate heat capacity for liquid components at an arbitrary temperature we can use the following known correlation:

$$Cl(T_l) = A + BT_l + CT_l^2. \quad (11)$$

Constants A, B, C for different substances are listed in the tables [5].

Heat capacities of gases and vapors will change during a technological process run depending on the pressure. As heat capacity is connected with enthalpy by the correlation

$$C_p = (\partial H / \partial T)_p, \quad (12)$$

heat capacity change by pressure change can be written in the following form:

$$\frac{C_p - C_p^0}{R} = -\frac{\partial}{\partial T_p} \left[\int_0^{P_p} T_p^2 \left(\frac{\partial Z}{\partial T_p} \right)_{P_p} d(\ln P_p) \right]_{P_p}. \quad (13)$$

The last equality after transformation leads to the equation

$$\left(\frac{\partial C_p}{\partial P} \right)_T = \frac{\partial^2 H}{\partial P \partial T} = \frac{\partial}{\partial T} \left[\left(-\frac{RT}{P} \right)^2 \cdot \left(\frac{\partial Z}{\partial P} \right)_p \right]_{P_p}. \quad (14)$$

Here we additionally assume that at a constant pressure heat capacities of gases and vapors practically do not depend upon temperature.

A differential equation of material balance can be derived for separate components of the mixture. The material balance equation for the first i component of a vapor and gas mixture has the following form:

$$I_{IIi} S_{CB} \cdot d\tau - I_{II2i} C_{ni} \cdot d\tau = V_{CB} \cdot dC_{ni}. \quad (15)$$

The first member in equation (15) reflects the inlet of the vapor mixture i component to the curing chamber due to vaporization of i liquid component from the surface of the treated material, the second component is the inlet of the vapor mixture i component to the trapping system. The right part of equation (15) characterizes a change in partial concentration of i component in a vapor mixture.

A material balance equation for j component of a vapor and gas mixture can be written in a similar form:

$$I_{I1j} S_{CB} \cdot d\tau - I_{I2j} C_{Ii} \cdot d\tau = V_{CB} \cdot dC_{Ij}. \quad (16)$$

The components of the last equality correspond in a qualitative form to equation (15).

Equations (15), (16) contain the values of volumetric capacity characterizing a system for toxic emission trapping according to different vapor and gas components. In general, connection of volumetric capacity with concentration can be expressed by power dependence

$$I_{II2i} = \frac{C_i I_{2\Sigma}}{M_i \left(\sum_{j=1}^m \frac{C_j}{M_j} + \sum_{i=1}^n \frac{C_i}{M_i} \right)}, \quad I_{2\Sigma} = AP^n. \quad (17)$$

Moreover, equations (15), (16) also contain the values of gas and vapor flows for I_{IIi}, I_{I1j} components that can be calculated in the following way. We can assume that a set of liquid components contained in the treated material is an ideal system. Then the partial pressures of vapor components close to the surface of the treated material can be written according to the Raoult law for ideal systems:

$$P_i = X_i P_{0i}. \quad (18)$$

In accordance with the earlier accepted assumptions, the vapor pressure of a pure component is calculated by the Antoine equation

$$P_{0i} = \ln(A_i - B_i/T). \quad (19)$$

By insertion of equation (19) into (18) we deduce a formula for calculation of partial pressures for vapor components over the surface of the treated material at an arbitrary temperature:

$$P_i = X_i \ln(A_i - B_i/T). \quad (20)$$

Differentiation of both parts of equation (20) leads to a formula for calculation of partial pressure increments for vapor components over the material surface by dT temperature change:

$$\Delta P_i = \frac{X_i B_i \ln(A_i - B_i/T)}{T^2} \cdot dT + X_i \ln(A_i - B_i/T). \quad (21)$$

According to the earlier accepted assumptions, the components of a gas and vapor mixture obey the ideal gas laws. Therefore, partial density of the vapor and gas mixture components over the material surface can be found by the Mendeleev – Clapeyron equation

$$\rho_i = P_i M_i / RT. \quad (22)$$

Differentiation of both parts of equation (22) leads to the following equation:

$$d\rho_i = \frac{M_i}{RT} \cdot dP_i - \frac{P_i M_i}{RT^2} \cdot dT. \quad (23)$$

By insertion of the form (21) into (23) we derive a form for calculation of partial density increments for vapor components over the material surface by dT temperature change:

$$d\rho_i = \frac{M_i}{RT} \left[\frac{X_i B_i \ln(A_i - B_i/T)}{T^2} \cdot dT + \right] - \frac{M_i}{RT^2} \cdot dT \cdot X_i \ln(A_i - B_i/T). \quad (24)$$

Formula (24) contains mole fraction of X_i component. For its determination we will make the following calculations.

We define the partial mass decreasing due to vaporization for i liquid component contained in the treated material:

$$m_i = m_{iD} - S_{SB} \int_D^\tau I_{\Pi i}(\tau) \cdot dx. \quad (25)$$

Mole fraction of i component is expressed through its partial mass by the following correlation:

$$X_i = \frac{m_i}{M_i \left(\sum_{j=1}^n \frac{m_j}{M_j} + \sum_{i=1}^m \frac{m_i}{M_i} \right)}. \quad (26)$$

It possible to express the mass of vapors i component through density and volume:

$$m_i = \rho_i V. \quad (27)$$

Time differentiation in the left and right parts of equation (27) and division by the surface area of the treated material lead to the following equation:

$$\frac{1}{S} \cdot \frac{dm_i}{d\tau} = \frac{V}{S} \cdot \frac{d\rho_i}{d\tau}. \quad (28)$$

As the height, volume and cross section area of the chamber are connected by the correlation $H = V/S$, and the left part of equation (28) is the flow of the i vapor component, this equation can be transformed as follows:

$$I_{\Pi i} = H \cdot \frac{d\rho_i}{d\tau}. \quad (29)$$

Inserting formula (24) into (29), it is possible to derive an equation for calculating partial vapor flows released from the surface of the treated material:

$$I_{\Pi i} = \frac{H}{d\tau} \left[\frac{M_i}{RT} \left[\frac{X_i B_i \ln(A_i - B_i/T)}{T^2} \cdot dT + \right] \right] \cdot \left[\frac{M_i}{RT^2} \cdot dT \cdot X_i \ln(A_i - B_i/T) \right]. \quad (30)$$

$I_{\Gamma 1j}$ partial flow of j gas component included into formula (16) is defined in the following way. The kinetic equation of a reaction taking place inside or on the surface level of the treated material is written in the following form:

$$W = k C_{li}^{\phi_i} C_{lk}^{\phi_k}. \quad (31)$$

The dependence of the chemical reaction constant speed upon temperature is determined by the Arrhenius law

$$k = Z \ln(-E/RT). \quad (32)$$

Taking into account that the vaporization intensity is proportional to the chemical reaction speed and the surface area of the treated material, we finally deduce:

$$I_{\Gamma 1j} = Z \ln(-E/RT) \cdot C_{li}^{\phi_i} \cdot C_{lk}^{\phi_k} \cdot S_{mat}. \quad (33)$$

5. Mathematical modeling of processes taking place with gas emissions of big quantities

In this case heat balance equations will be similar to those for processes taking place with gas emissions of small quantities. Equations for material balance will also be similar to the equation for slow flowing processes, but here it is more convenient to use as a variable partial density of the vapor and gas mixture component. It is implied by the fact that in this case by contrast to the previous one it is not possible to neglect the resistance of liquid and gas phases. Therefore, to calculate the flows of gas and vapor components from the surface of the treated material we use the following equation:

$$I_i = -\beta_i (\rho_i - \rho_i^*). \quad (34)$$

To sum it up, a material balance equation for the first i vapor component has the following form:

$$I_{\Pi i} \cdot S_{CB} \cdot d\tau - I_{\Gamma 2i} \cdot \rho_{\Pi i} \cdot d\tau = V_{CB} \cdot d\rho_{\Pi i}. \quad (35)$$

A material balance equation for the first j gas component is:

$$I_{\Gamma 1j} \cdot S_{CB} \cdot d\tau - I_{\Gamma 2j} \cdot \rho_{\Gamma j} \cdot d\tau = V_{CB} \cdot d\rho_{\Gamma j}. \quad (36)$$

To formulate a constructive mathematical description of the processes it is reasonable to make a number of assumptions.

In accordance with the assumptions accepted earlier, the i component density close to the surface of the treated material ρ_i^* can be considered as an equilibrium value, i.e. a value uniquely defined by the state of a liquid phase. The i component density for camera volume ρ_i can be found from balance equations.

The physical meaning of additives from equations (35) and (36) is similar to that of corresponding additives from equations (15), (16). Just like in the case with processes taking place with gas emissions of small quantities, volumetric capacity of a system for trapping toxic emissions is connected for the first vapor and gas mixture i component with its concentration through power dependence.

Partial pressures of the gas and vapor mixture components are connected with their weight concentrations according to the known formula [6].

Equations (35), (36) contain the partial flow values of vapor $I_{\Pi i}$ and gas $I_{\Gamma 1j}$ components. Vapor flows

$I_{\Pi i}$ can be calculated according to the following formula:

$$I_{\Pi i} = -\beta_{\Pi i} (\rho_{\Pi i} - \rho_{\Pi i}^*). \quad (37)$$

According to the earlier accepted assumptions, the components of a gas and vapor mixture obey the ideal gas laws. That is why partial density of a vapor component close to the surface of the treated material can be found by the Mendeleev – Clapeyron equation:

$$\rho_i^* = \frac{P_i^* M_i}{RT}. \quad (38)$$

Similarly to the processes taking place with gas emissions of small quantities partial pressures of vapor components over the surface of the treated material can be calculated according to the formula:

$$P_i^* = X_i \ln(A_i - B_i/T^*). \quad (39)$$

Choosing a considerably thin layer over the surface of the phase border with the account of temperature continuity in space we can deduce the border temperature condition of the first genus for the phase border:

$$T^* = T_{\mathcal{K}}. \quad (40)$$

Inserting (39) into (38) and taking into consideration the border condition (40), we will have:

$$\rho_i^* = \frac{M_i}{RT} \cdot X_i \cdot \ln(A_i - B_i/T_{\mathcal{K}}). \quad (41)$$

By insertion of (41) into (37) we derive a formula for calculation of partial vapor flows:

$$I_{\Pi i} = -\beta_{\Pi i} \left(\rho_{\Pi i} - \frac{M_i}{RT} \cdot X_i \cdot \ln(A_i - B_i/T_{\mathcal{K}}) \right). \quad (42)$$

Partial densities $\rho_{\Pi i}$ included into formula (42) are defined from the material balance equation (35). Mole fractions of the liquid components X_i are calculated in a similar way as for slow flowing processes, i.e. according to formulas (25), (26).

Partial flow of j gas component released from the surface of the treated material is also calculated for slow flowing processes according to formula (33).

Due to complexity of the derived equation system it is not possible to give a solution for it in an explicit form. That is why we use the numerical method of finite differences for approximation of the set.

6. Physical model of multicomponent gas absorption

At the premises of OJSC Tyre Enterprise „Amtel – Tchernosemye“ a trial industrial aggregate was designed for investigation of curing gas absorption where an alkaline solution was used as an absorbent.

To get more precise data on the degree of absorption intensification by temperature increase it is necessary to formulate an experimental dependence of the system productivity used for trapping of gases and vapors released

in the curing process upon their concentration in the chamber. As to measure the productivity of the trapping system directly is considerably difficult, in this work we used an indirect method for productivity evaluation based on the following factors.

If the change in the mass concentration of j component is known for some time period, then it is possible to calculate the component mass change in the chamber caused by running a vapor and gas trapping system according to the formula:

$$\Delta m_j = \Delta C_j V_k. \quad (43)$$

Then knowing the density of j component ρ_j we can estimate the change in this component volume according to the following formula:

$$\Delta V_j = \Delta m_j / \rho_j = \Delta C_j V_k / \rho_j. \quad (44)$$

Division of the value ΔV_j by the time period $\Delta \tau$ leads to the volumetric capacity of the gas and vapor trapping system for j component

$$J_j = \Delta V_j / \Delta \tau = \Delta C_j V_k / \rho_j \Delta \tau. \quad (45)$$

Considering mass concentrations (kg/m^3), this formula can be written in the following form:

$$J_j = \Delta C_j V_k / C_j \Delta \tau. \quad (46)$$

Using formula (46) it is possible to formulate dependence of the trapping system volumetric capacity for j component upon the concentration of this component in the curing gas emission chamber.

Table 1 lists the experimental data of the dynamic change in the concentration of aromatic hydrocarbons released during tyre curing and the volumetric system capacity calculated according to formula (46).

Fig 1 shows dependence of aromatic hydrocarbon concentrations, sulphur organic compounds and aldehydes in the curing chamber upon the process duration.

Table 1. Concentration changes of aromatic hydrocarbons released during curing

Characteristics	Process duration, min			
	6	12	18	24
Aromatic hydrocarbon-concentration, mg/m^3	850	1400	1740	1950
Mass concentration change, $(\text{mg}/\text{m}^3)/\text{s}$	150	300	510	640
Trapping system capacity, m^3/s	0,18	0,36	0,612	0,768

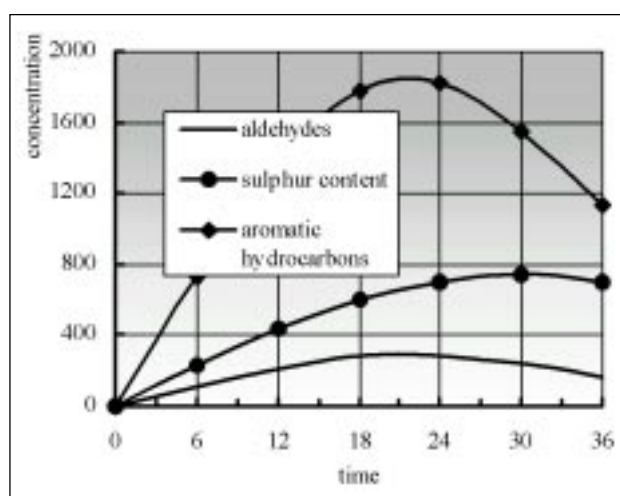


Fig 1. Dependence of gas concentrations in the curing chamber on process duration

The received data evidence that the process of trapping released gases and vapors gets more intensive with increase of their concentration in the curing chamber. A check for the mathematical model adequacy has shown that the difference between the calculation and experimental data is within a confidence interval.

A graphic analysis in Fig 1 shows that there are two concentration-time dependences which are sharply defined. In the first period the concentration of gases and vapor in the chamber increase, as this period coincides with the curing cycle. An increase in the gas and vapor contents is also observed in an adjoining 2 m work zone (Fig 2).

In the second period there is a decrease in the concentration of released gases and vapor, since the trapping system is in operation. Accordingly, the component concentrations in a 2 m work zone decrease.

It is typical that dependences of the component concentration changes in the first period as well as in the second one have exponential characteristics. It is explained by the fact that the trapping system capacity increases with

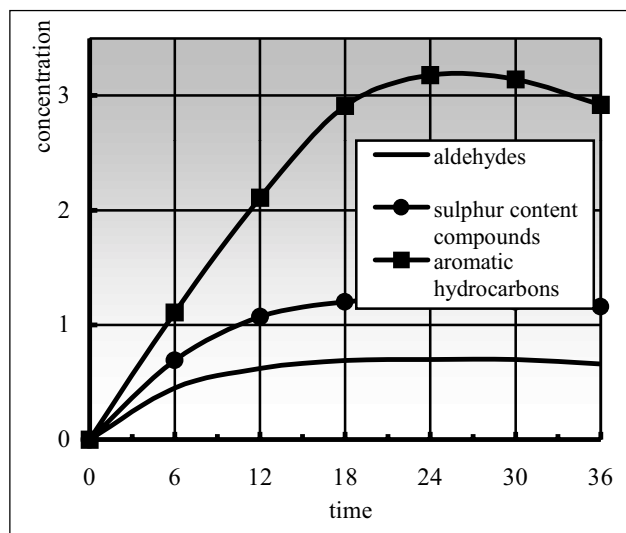


Fig 2. Dependence of curing gas concentrations in the work area on process duration

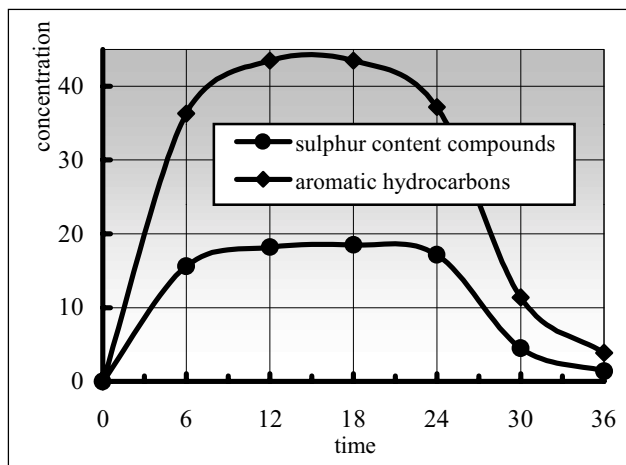


Fig 3. Dependence of curing gas concentrations on curing duration with their slow release in the chamber

increase of trapped gas concentrations according to the power law. As a result, at the beginning of the curing process the change in the concentrations of gas emissions is nearly linear. As the concentration of released gases and vapor increases, the system capacity grows, and the component concentration in the chamber drops to certain values: for aromatic hydrocarbons – to 1995 mg/m^3 , for sulphur content compounds – to 584 mg/m^3 and for aldehydes – to 161 mg/m^3 . At the beginning of the second period the concentrations of gas components reach maximum values, and at the same time the trapping system works more efficiently. As the concentration of harmful gases and vapor drops in the chamber, the efficiency of the trapping system decreases, and the curves of the concentration-time dependence gradually approach the zero level. In this zone the curves have the characteristics of decreasing exponents.

In order to check, if it is possible to describe gas emissions during tyre curing by the elaborated mathematical methods and algorithms, an experimental investigation took place using an aggregate by 260–508 P truck tyres curing in the curing press $\Phi B-200$.

The mode parameters of the curing processes and the test changed within the following limits: the curing temperature was kept at the level of $150\text{--}160 \text{ }^\circ\text{C}$, duration of the curing process was 45 min, the absorbent temperature changed within the limits of $16\text{--}18 \text{ }^\circ\text{C}$, water concentration amounted to $25 \text{ m}^3 / (\text{m}^2 \cdot \text{hour})$. The quantitative composition of released harmful gases and vapor was estimated by chromatographic analysis of samples selected at the line for the outlet of gas flow from the hermetic housing to the absorber.

The processes of forming and trapping of harmful emissions with a slow release were studied during flap component curing. Fig 3 shows dependence of vapor concentration of aromatic hydrocarbons and sulphur content compounds in the chamber upon curing duration.

It is clear that the concentration-time dependence, as in the case of effervescence, has two periods in the form of increasing and decreasing exponents. Such a characteristic of released vapor concentration changes in the chamber is explained by the fact that in the second period, after curing is complete, the intensity of volatile emissions decreases rapidly due to a small weight of the flap.

7. Conclusion

The obtained mathematical models can serve as a basis for elaborating an engineering method for the design of industrial aggregates used for trapping curing gas releases with further decontamination or recuperation.

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ADSORBCIJOS PROCESO, UTILIZUOJANT PADANGŲ GAMYBOS METU SUSIDARIUSIAS VULKANIZACIJOS DUJAS, EFEKTYVUMO TYRIMAI

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S a n t r a u k a

Nagrinėjamas adsorbcijos proceso, utilizuojant vulkanizuotų padangų bei jų komponentų gamybos metu susidariusias dujas, matematinis bei fizinis modeliavimas. Pateikiama intensyvaus bei nežymaus dujų išsiskyrimo matematinų modelių sintezė bei analizė. Aprašyta adsorbcijos schema, formulėmis išreikšta eksperimentiniu būdu nustatyta produktyvumo priklausomybė nuo emisijų koncentracijos vulkanizacijos dujų emisijų ir garų sugaudymo sistemos absorbcinėje kameroje.

Raktažodžiai: padangos, vulkanizacijos dujos, lakieji junginiai, utilizacija, adsorbcijos procesas.

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Research interests: assembling/adhesive formulation, tread strip, adhesive film, air-stream carrying interlayer, adsorption.