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INVESTIGATION OF GAS RELEASE FROM MOLDS

G. Ya. Gerasimov[a] **and Yu. M. Pogosbekyan**[b]

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A mathematical model of gas release from a mold in the stage of solidification and cooling of metal has been constructed. The model includes heat and mass transfer on the mold's capillary-porous medium containing phenol-formaldehyde resin as a binder; it also includes the kinetics of pyrolysis of the resin and secondary chemical reactions between the products formed. The process has been investigated experimentally. It has been shown that the model gives a fairly good description of the process in a wide range of variation in its parameters within the framework of the assumptions made.

The process of gas release from molds is mainly responsible for the gas pollution of foundries. The level of gas pollution exceeds maximum permissible concentrations in some cases, which reduces labor productivity and poses social threats. They primarily include the environmental-pollution problem, when it is considered that engineering plants are located within the boundaries of large cites [1].

The content of toxic components (phenol, formaldehyde, polycyclic aromatic hydrocarbons, etc.) in molding gases has increased recently because of the wide use of different synthetic resins in mold production [2]. The high-temperature destruction of synthetic resins in the presence of chlorine compounds gives rise to polychlorinated dioxins which belong to the most toxic chemical substances [3].

Synthetic resins used in foundry are high-molecular-weight organic compounds whose thermal properties are determined by the chemical composition of monomers involved and by the type of bonds between them [4]. Investigations in this field are mainly associated with studying the mechanics of depolymerization at high temperatures [5–9].

The mechanism of thermal decomposition (pyrolysis) of resins entering into the composition of a molding sand (mixture) differs from the corresponding mechanism obtained under laboratory conditions because of the presence of secondary chemical reactions between the products formed. Therefore, calculation of gas release from a mold must include the entire set of physicochemical processes occurring in the mold in its contact with liquid metal. The available mathematical models for calculation of the parameters of the overall process are, conversely, semiempirical in character and do not describe its basic features under different technological conditions [10].

In the present work, an effort has been made to construct the most complete mathematical model of gas release from a mold with allowance for the presence of heat and mass transfer in a capillary-porous medium containing synthetic resin as a binder and for the kinetics of pyrolysis of the resin and secondary chemical reactions between the products formed. To verify the model we carried out experimental investigations on determination of the rates of release of molding gases from the sand based on the most toxic phenol-formaldehyde resin. The results of calculations using the model may provide the basis for prediction of the pollution of foundries with molding gases.

Experimental. The parameters of gas release in the case of solidification of liquid metal in a mold were measured with a device described in [11]. It contained the heat-insulated upper half-mold incorporating a cavity for casting with liquid metal and the lower half-mold incorporating a heat-insulated cylinder filled with the molding sand under study. The sand was fixed at the bottom using a grid below which there was a cavity where the molding gases released from the sand mixed with the carrier gas (e.g., argon). The flow rate of the carrier gas was monitored by a flow transducer precalibrated for the given gas. The running time was reckoned from the instant of the beginning of the process of casting of liquid metal into a mold.

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[a] Institute of Mechanics, M. V. Lomonosov Moscow State University, 1 Michurinskii Prospekt, Moscow, 119192, Russia; email: gerasimov@imec.msu.ru; [b] Moscow Automobile-Road Institute, 64 Leningradskii Prospekt, Moscow 125319, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 80, No. 3, pp. 112–120, May–June, 2007. Original article submitted February 10, 2006.

During the experiments, we casted gray cast iron into a mold. The casting thickness δ and the mold-wall thickness h varied within 3–40 mm and 15–200 mm respectively. The temperature of the casted gray cast iron changed from 1560 to 1690 K. The molding sands under study were prepared from 1K02B quartz sand and PK-104 phenol-formaldehyde resin (pulverbakelite) as a binder. The concentration of the resin in the sand changed from 2 to 8 mass %.

The mass rate of release of molding gases was calculated from the flow rate of the carrier gas and the concentration of the molding gases contained in the selected samples of the gas mixture. The chemical composition of the mixture was determined by chromatographic and gas-analytical methods. The basic measured parameter of the process was the released-gas volume $Q = Q(t)$ reduced to normal conditions. The relative coefficient of gas release $a = Q/t^{1/2}$, which was the most generalized characteristic of the gas-generating properties of any molding sands, was computed from the Q values [12].

Kinetics of Thermal Destruction of Resin. The process of degradation of synthetic resins in heating is described by numerous kinetic reactions. Nonetheless, all resins may be subdivided into two groups depending on the character of breaking of chemical bonds [9]. The first group includes resins whose depolymerization is determined by the breaking of bonds of the main chain to form low-molecular-weight volatiles. This group may include carbamido-formaldehyde resins widely used in mold production [2]. The second group includes resins prone to intramolecular splitting-out of corresponding functional groups and to cyclization and condensation reactions which give rise to numerous carbonized nonvolatiles. This group includes phenol-formaldehyde and furane resins. Thermal decomposition of resins in both the first and second groups may proceed by a radical, ionic, or molecular mechanism in a chain or non-chain manner [5].

Phenol-formaldehyde resins are synthesized in the polycondensation of phenol with formaldehyde to form a linear (novolac resin) or branched (resole resins) polymer [4]. The mechanism of thermal destruction of these resins has been much studied; the possible intermediate decomposition products and reactions between them are being refined at present (see, e.g., [13, 14]). It has been established that all the resins of the given class decompose nearly in the same manner, once they have completely hardened. Irrespective of whether destruction occurs in an oxidizing or inert medium, the process is always of a thermooxidative character because of the high content of oxygen in the resin [15].

In the first stage of thermooxidative destruction of phenol-formaldehyde resins ($T < 600$ K), the polymer changes only slightly and the number of gaseous decomposition products released is small. In the temperature interval 600–900 K, the destruction rate grows sharply. In this stage of the process, the resin is yet to be depolymerized completely; there can be only a random splitting of polymer chains to form carboxyl (-COOH), carbonyl (>C=O), and methyl ($-CH_3$) functional groups whose splitting-out gives rise to light gas components: CO_2, CO, and CH_4. At the same time, we have a separation of large molecular fragments with the oligomer fraction (OF) reaching the gas phase. On the basis of the average molecular weight of the fraction ($\mu_{OF} = 340$), it is believed that the fraction consists of the fragments of the resin's three-dimensional structure, i.e., oligomers averaging three to four benzene rings [16]. In the third stage of destruction ($T > 900$ K), the polymer undergoes deeper changes accompanied by the transformation of phenols into condensed carbon [17].

Despite the considerable progress made in understanding the mechanisms of pyrolysis of different resins, modeling of the process is confined, as a rule, to the simplest kinetic models describing conversion of the starting polymer as a whole without concrete definition of the products formed (see, e.g., [18, 19]). In a number of models, use is made of the probabilistic approach to consideration of the process, in which the depolymerization of resin is represented as a random disintegration of macromolecules of different length into smaller components (see, e.g., [20]). Such models are suitable for modeling of the decomposition of polymers with a low yield of condensed carbon.

In the present work, we have used the functional-group model [21] to describe the behavior of phenol-formaldehyde resin at high temperatures. In accordance with the above-described mechanism of the process, the resin may be presented as a condensed aromatic structure containing different functional groups (carboxyl, carbonyl, methyl groups, and others) in the form of substituents. Bonds attaching the functional groups to aromatic rings are broken in rapid heating of the resin to form gas volatiles. At the same time, we have a splitting of polymer chains with the reaching of the gas phase and the residue being carbonized. The aromatic hydrogen released goes to stabilize free radicals and to form H_2.

In the functional-group model, the component reaching the gas phase is described by the system of kinetic equations

TABLE 1. Kinetic Parameters of Yield of the Functional Groups from Phenol-Formaldehyde Resin

Group	Y_{i0}	A_i, sec^{-1}	E_i, kJ/mole
OF	0.289	4	58.24
CO	0.140	$2 \cdot 10^2$	99.81
CH_4	0.040	$4 \cdot 10^4$	124.81
H_2	0.028	$6 \cdot 10^6$	191.34
CO_2	0.012	$1 \cdot 10^2$	74.86

TABLE 2. Experimental [16] Mass Concentrations of Volatiles in the Thermodestruction Products of Phenol-Formaldehyde Resin and Those Calculated in the Present Work (given in brackets)

Group	t = 3600 sec	t = 1800 sec	t = 300 sec	
	Temperature of the process, K			
	633	773	1073	1473
OF	0.083 (0.057)	0.140 (0.160)	0.262 (0.233)	0.180 (0.280)
CO	—	0.010 (0.010)	0.071 (0.080)	0.118 (0.140)
CH_4	—	0.012 (0.009)	0.055 (0.040)	0.043 (0.040)
H_2	—	—	0.016 (0.016)	0.027 (0.028)
CO_2	0.001 (0.003)	0.015 (0.010)	0.012 (0.012)	0.010 (0.012)

$$dY_i/dt = -k_i Y_i\,, \quad k_i = A_i \exp\left(-\frac{E_i}{RT}\right), \quad Y_i\Big|_{t=0} = Y_{i0}\,. \tag{1}$$

In the present work, the kinetic parameters of the model (A_i, E_i, and Y_{i0}) as applied to the pyrolysis of phenol-formaldehyde resin have been obtained by fitting the calculated curves describing the dynamics of the process under isothermal conditions to experimental data [16]. Table 1 gives the values of the above quantities for the basic functional groups of the resin participating in the formation of the gas phase. The concentration of condensed carbon (carbon residue) is $Y_C = 0.5$. The activation energy of the reaction of H_2 yield has been taken to be equal to the corresponding quantity for thermal decomposition of the organic coal mass [22] because of the shortage of experimental data.

Table 2 compares the computed values of the quantities ($Y_{i0} - Y_i$) and experimental results [16]. The agreement is fairly good, on the whole. The appreciable difference for the OF at T = 1473 K is attributable to the possible decomposition of the OF vapor before its condensation in the low-temperature part of the device. It is noteworthy that, under actual conditions, the gas phase contains a much larger number of components, in particular, acetylene, ethylene, acetone, propanol, benzene, and others [16]. Some of them are the products of thermodestruction of the resin; others are formed in secondary chemical reactions. The molar concentrations of these components are low, as a rule, and they have no substantial influence on the dynamics of the process.

Secondary Chemical Reactions. Intense decomposition of phenol-formaldehyde resin in a molding sand occurs at temperatures of the order of 1000–1200 K [12]. The volatile decomposition products migrate thereafter in the capillary-porous medium, undergoing different secondary reactions, mainly cracking, condensation, and polymerization of the OF with deposition of a certain amount of carbon [23]. The cracking of the OF vapor is primarily determined by the rupture of methylene bonds between the benzene rings. Therefore, in the simplest case we may confine ourselves to a mixture of phenol and methane for modeling of the subsequent transformation of the OF-disintegration products.

Quite detailed kinetic mechanisms of combustion of aromatic hydrocarbons, including phenol, are available at present [24, 25]. In a neutral medium, the high-molecular transformation of phenol may be represented by a chain of reactions of formation of the peroxide radical C_6H_5O with its subsequent transformation to the cyclopentadienyl radical *cy*-C_5H_5, the opening of the cycle, and the formation of the propargyl radical C_3H_3 [26]:

TABLE 3. Kinetic Mechanism of High-Temperature Transformation of Phenol in an Inert Medium

Reaction	log A	n	E, kJ/mole	Reference
$OF \rightarrow C_6H_5OH + CH_4$	13.00	—	272.14	[30]
$C_6H_5OH \rightarrow C_6H_5O + H$	16.43	—	371.96	[31]
$C_6H_5O cy\text{-}C_5H_5 + CO$	11.87	—	183.63	[32]
$cy\text{-}C_5H_5 \rightarrow C_5H_5$	13.87	—	139.42	[33]
$C_5H_5 \rightarrow C_3H_3 + C_2H_2$	14.00	—	71.18	[34]
$C_3H_3 + C_3H_3 \rightarrow A_1$	12.70	—	—	[35]
$C_3H_3 + H \rightarrow C_3H_4$	13.30	—	—	[34]
$C_6H_5 \rightarrow C_4H_3 + C_2H_2$	15.20	—	343.32	[36]
$C_4H_3 + H_2 \rightarrow C_4H_4 + H$	10.20	—	74.15	[36]
$C_4H_4 \rightarrow C_2H_2 + C_2H_2$	15.06	—	362.24	[37]
$A_k\bullet + C_2H_2 \rightarrow A_kC_2H_2\bullet$	38.85	–8.02	68.66	[35]
$A_kC_2H_2\bullet + C_2H_2 \rightarrow A_{k+1} + H$	16.20	–1.33	22.61	[35]
$A_k\bullet + C_4H_4 \rightarrow A_{k+1} + H$	33.52	–5.70	106.76	[35]
$A_k \rightarrow$ products	7.82	—	200.00	[38]

Note. The rate constant is $k = AT^n \exp(-E/RT)$ $(\text{cm}^3\cdot\text{mole}^{-1})^{m-1}\text{sec}^{-1}$.

$$C_6H_5OH \xrightarrow{-H} C_6H_5O \xrightarrow{-CO} cy\text{–}C_5H_5 \rightarrow C_5H_5 \rightarrow C_3H_3 + C_2H_2\,. \tag{2}$$

The recombination of propargyl radicals is the basic channel of formation of benzene. The structural buildup of aromatic molecules and their condensation to soot particles is a complex physicochemical process [27]. The simplest model of the process includes the formation of aromatic radicals $A_k\bullet$ and further addition of acetylene molecules to them [28]:

$$A_k + H \xrightarrow{-H_2} A_k\bullet \xrightarrow{H_2C_2} A_kC_2H_2\bullet \xrightarrow{H_2C_2} A_{k+1}\,. \tag{3}$$

In the present work, we have used the kinetic mechanism of oxidation of benzene and its derivatives [29] to model the high-temperature transformation of phenol in the medium of volatile prodicts of destruction of phenol-formaldehyde resin; the mechanism consisted of 130 elementary chemical reactions and was supplemented with the reactions entering in the chains (2) and (3) whose kinetic parameters are given in Table 3.

The volatiles that have escaped in the pyrolysis of the resin move thereafter in the pore space of the mold to its external boundary, arriving at the region of lower temperatures. The condensation and repolymerization of the unreacted part of the OF with the formation of a carbon residue and the volatile repolymerization product reaching the gas phase occur. It is quite difficult to mathematically describe their process in detail. In the simplest case it may be allowed for by direct addition of CO and H_2 to the gas phase and C to condensed carbon; the amount of the substances added is determined based on an analysis of the OF element composition.

Processes of Heat and Mass Transfer. In the course of the process of solidification of metal in the mold, the amount of the solid phase increases, whereas the amount of the liquid phase decreases. We recognize three zones in the solidifying casting: a solidified layer, a two-phase zone (liquid metal and metal crystals), and a liquid layer. The crystallization rate and accordingly the increase in the solidified-metal thickness are determined by the thermal regime of a mold, which also influences the quality of the casting: the grain size, the presence of fractures and blow-holes, etc. [39].

Let us consider the model problem of molding a casting in a dry mold in one-sided heat removal through the mold wall. We assume that the temperature of a liquid metal in the process of its crystallization is constant and the overheating of the metal in casting into the mold is insignificant. Since the concentration of resin in the sand is low, we will assume that the thermal effect of pyrolysis reactions, the convective transfer of heat by the gas components, and the influence of the change in the sand mass on the formation of a temperature field may be disregarded. Then the heat-conduction equation in a one-dimensional formulation will take the form

$$\rho_{\text{mix}} c_{\text{mix}} \frac{\partial T}{\partial t} = \lambda_{\text{mix}} \frac{\partial^2 T}{\partial x^2} . \tag{4}$$

In the case of solidification of metal in the mold the equation for determination of the quantity ξ $(0 \le \xi \le \delta)$ and the boundary condition on the metal–mold interface are as follows:

$$\rho_{\text{m}} H_{\text{m}} \frac{d\xi}{dt} = - \lambda_{\text{mix}} \left. \frac{\partial T}{\partial x} \right|_{x=0} ; \quad T(t, 0) = T_{\text{m}0} . \tag{5}$$

In cooling of the solidified metal, the equation describing the change in T_{m} and the boundary condition on the interface are written in the form

$$\rho_{\text{m}} c_{\text{m}} \delta \frac{dT_{\text{m}}}{dt} = \lambda_{\text{mix}} \left. \frac{\partial T}{\partial x} \right|_{x=0} ; \quad T(t, 0) = T_{\text{m}} . \tag{6}$$

The corresponding boundary condition at the external boundary of the mold is specified by the relation

$$- \lambda_{\text{mix}} \left. \frac{\partial T}{\partial x} \right|_{x=h} = \alpha \left[T(h, t) - T_{\text{a}} \right] + \varepsilon\sigma \left[T^4 (h, t) - T_{\text{a}}^4 \right] . \tag{7}$$

The initial conditions are as follows: $\xi(0) = 0$ and $T(x, 0) = T_{\text{a}}$. The thermal conductivity, heat capacity, and density of molding sands for the prescribed composition and degree of compaction are determined experimentally. In particular, for the sand under study we have $\lambda_{\text{mix}} = 0.7$ W/(m·sec), $c_{\text{mix}} = 1200$ J/(kg·K), and $\rho_{\text{mix}} = 1600$ kg/m^3 [39]. For gray cast iron, we have $\rho_{\text{m}} = 6900$ kg/m^3, $H_{\text{m}} = 240$ kJ/kg, and $c_{\text{m}} = 540$ J/(kg·K).

The filtration of volatile products of resin pyrolysis in the capillary-porous medium of the mold is described by the continuity equation [40, 41]

$$\frac{\partial (\rho \varepsilon_{\text{mix}} y_i)}{\partial t} + \frac{\partial N_i}{\partial x} = R_i , \tag{8}$$

$$N_i = y_i N , \quad R_i = \rho_{\text{mix}} \varphi_{\text{mix}} G_i (x, t) ,$$

$$G_i (x, t) = Y_{i0} A_i \exp \left\{ - \frac{E_i}{RT (x, t)} - A_i \int_0^t \exp \left[- \frac{E_i}{RT (x, t)} \right] dt \right\} .$$

The expression for $G_i(x, t)$ is obtained by integration of the kinetic equation (1). Since the mass-mean gas velocity in the medium $v = N/(\rho\varepsilon_{\text{mix}})$ is much smaller than the velocity of sound, in considering gas flow we may confine ourselves to the quasistationary regime and may disregard the first term in Eq. (8).

The mass fluxes N_i entering in Eq. (8) are generally dependent on the concentration gradient y_i and the pressure gradient p [40]. For the process in question, the influence of diffusion of the gas components on N_i is insignificant; the mass flux of pyrolysis products due the the pressure difference plays a dominant role. In this case the pressure and density of the gas in the medium are determined from the equations

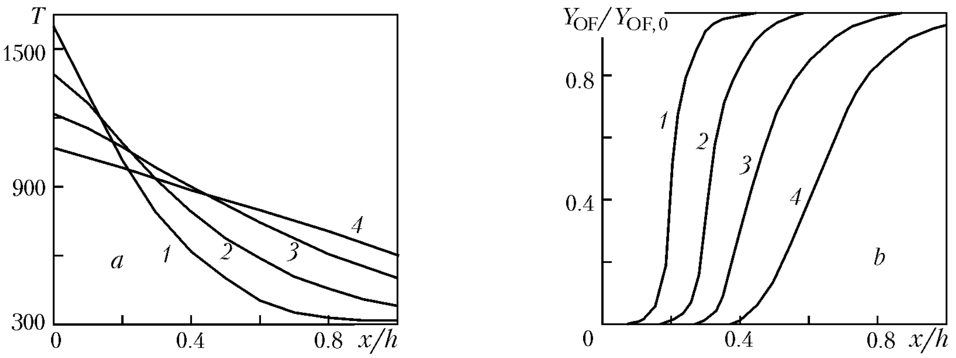
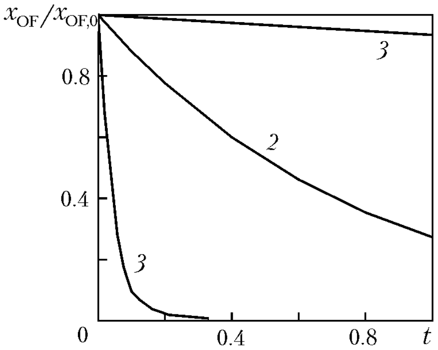


Fig. 1. Calculated distributions of the temperature (a) and concentration of OF (b) in the mold: 1) $t = 400$, 2) 800, 3) 1600, and 4) 3200 sec. Parameters of the process: $h = 50$ mm, $\delta = 15$ mm, $T_{m0} = 1600$ K, and $T_a = 300$ K. T, K.



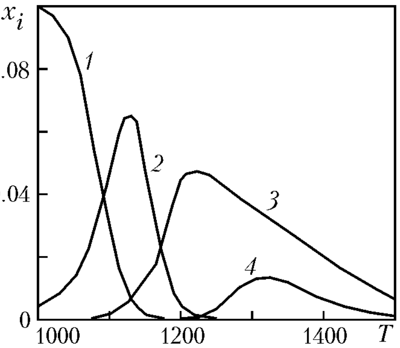


Fig. 2. Concentration of the OF vapor vs. time of its residence in the high-temperature region: 1) $T = 1000$, 2) 1100, and 3) 1200 K. t, sec.

Fig. 3. Temperature dependence of the concentrations of volatile aromatic components in the high-temperature region: 1) OF vapor; 2) phenol; 3) benzene (A_1); 4) naphthalene (A_2). The time of residence of the volatiles at a prescribed temperature is $t = 1$ sec. The parameters of the process are the same as those for Fig. 1. T, K.

$$N(x,t) = -\rho\varepsilon_{\text{mix}}\frac{r^2}{8\eta}\frac{\partial p}{\partial x}, \quad \rho(x,t) = \frac{p}{RT}(\Sigma_i y_i/\mu_i)^{-1}. \tag{9}$$

Boundary conditions for (8) and (9) with allowance for the assumptions made are written in the following form: $N_i(0, t) = 0$ and $p(h, t) = p_a$.

Results and Discussion. Experimental and numerical investigations of gas release from a mold in the stage of solidification and cooling of the casting have been carried out as applied to the actual conditions of the technological process in a wide range of variation in its parameters. As the calculations have shown, a dominant role in the dynamics of gas release is played by the formation of a temperature field in the mold. Figure 1a shows temperature curves calculated for the case of the average values of the casting δ and mold-wall thickness h. It is seen that, when the time of the process is $t < 400$ sec, the metal solidifies and the temperature of the mold layer adjacent to the casting is invariable. From the instant $t \sim 400$ sec, the casting begins to cool down, which leads to a reduction in the temperature of the left boundary of the mold. In calculating heat exchange with the environment (right boundary of the mold), we took $\alpha = 20$ W/(m^2·K) for the heat-transfer coefficient [42].

The pressure (calculated for $r = 5$ μm) in the zone adjacent to the casting first sharply increases to $p = 0.14$ MPa at $t = 10^{-2}$ sec and then decreases to $p = 0.103$ MPa at $t = 1$ sec, which is consistent with the data of [12]. It

TABLE 4. Comparison of Experimental and Calculated Data on Emission of a Molding Gas from a Mold at T_{m0} = 1600 K

φ_{mix}	δ, mm	*h*, mm	*t*, sec	*Q*, nm^3/m^2	
				experiment	calculation
0.04	18	15	300	0.468	0.415
		50	1080	0.789	0.749
		100	1680	0.861	0.893
	28	50	1200	0.866	0.914
		100	1800	0.976	1.130
0.06	10	15	300	0.728	0.528
	18	15	300	0.745	0.622
		50	1080	1.249	1.120
		100	1680	1.312	1.340
	28	50	1200	1.386	1.370
		100	1800	1.527	1.690
0.08	18	15	300	0.935	0.830
		50	1080	1.545	1.500
		100	1680	1.599	1.790
	28	50	1200	1.697	1.830
		100	1800	1.867	2.200

is noteworthy that the influence of pressure on the thermal decomposition of resin is insignificant [43]; this quantity is of importance only when the regime of filtration of volatiles in the mold's capillary-porous medium is established.

The pyrolysis of resin in the initial stage of the process occurs in a narrow zone whose width is $\Delta x/h < 0.1$ and the temperature is higher than 1200 K. In the course of the process, the pyrolysis zone approaches the external boundary of the mold; its width increases, whereas the temperature decreases, which is clear from Fig. 1b where the concentration curves $Y_{OF}(x, t)$ are shown. At the instant of time $t = 400$ sec, the OF intensely reaches the gas phase in the interval $0.15 \leq x/h \leq 0.25$, where the temperature T varies from 1200 K for $x/h = 0.15$ to 900 K for $x/h = 0.25$ (Fig. 1a). At the instant $t = 1600$ sec, the corresponding interval is equal to $0.5 \leq x/h \leq 0.8$, and the average temperature in it decreases to 700 K.

The data of calculating the temperature and concentration fields show that, in the initial stage of the foundry process ($t < 400$ sec), the volatiles that have escaped arrive at the region of high temperatures. Evaluation of the mass-mean gas velocity in the medium v for $\varepsilon_{mix} = 0.3$ yields a value of the order of 1 sec for the time of residence of the volatiles in this region. Figure 2 shows the behavior of the concentration of the volatiles' OF at different temperatures (for the same parameters of the process as those in Fig. 1). It is seen that the cracking of the OF vapor to form lighter gas components (phenol and methane in this case) begins at temperatures above 1000 K.

Figure 3 gives the kinetic curves of aromatic components of volatiles in the high-temperature region. An analysis of the figure shows that the OF concentration drops sharply with increase in the gas-medium temperature. The disintegration of OF molecules gives rise to phenol which thereafter changes to benzene followed by the structural buildup of the aromatic molecule. Thus, in the initial stage of the foundry process where the temperature in the pyrolysis zone is fairly high, we have a formation of aromatic (benzene, phenol) and polycyclic aromatic hydrocarbons whose concentration in the molding gas may be fairly high.

The results of measuring the volume of the released molding gases Q for different values of the parameters of the process and their comparison to calculated data are given in Table 4. The agreement of the results obtained is quite good for all the given variants. The measured average composition of the gases (H_2 = 50, CO = 36, CO_2 = 0.5, CH_4 = 7.5, O_2 = 0.3, and N_2 = 2.8 vol. %) differs somewhat from the calculated one (H_2 = 59, CO = 31, CO_2 = 1.3, and CH_4 = 8.7 vol. %) in that the mole ratio H_2/CO is smaller. It is clear from the table that the gas-formation intensity increases with resin content in the molding sand, all other things being equal. In the calculated data, this in-

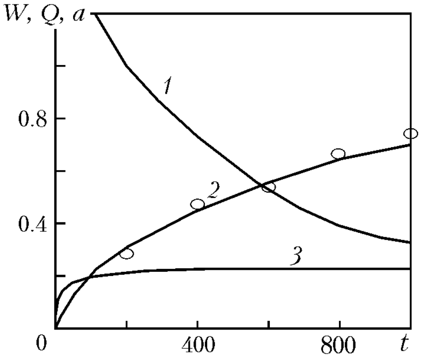


Fig. 4. Dependence of W, Q, and a on the time of the foundry process: 1) $W \cdot 10^3$; 2) Q; 3) $a \cdot 10$. Points, measurement data. The parameters of the process are the same as those for Fig. 1. W, $\text{nm}^3/(\text{m}^2 \cdot \text{sec})$; Q, nm^3/m^2; a, $\text{nm}^3/(\text{m}^2 \cdot \text{sec}^{1/2})$; t, sec.

crease is in proportion to φ_{mix}. Experimental values of the quantity Q grow somewhat slower. This is attributable to, first, the small increase in the porosity of the resin and accordingly the decrease in its density with φ_{mix}; second, the endothermal effect of thermodestruction of phenol-formaldehyde resin increases, which slows down the heating of the molding sand [12].

Figure 4 shows the behavior of the basic parameters of gas release W and Q as a function of the time of the foundry process. Also, the figure gives the calculated values of the relative gas-release coefficient $a = Q/t^{1/2}$. As is seen in the figure, in the initial stage of the process, we have a rapid growth in this coefficient with it reaching a constant value ($a = 0.023$ $\text{nm}^3/(\text{m}^2 \cdot \text{sec}^{1/2})$) at $t \geq 300$ sec. Consequently, the proposal expressed in [12] that this quantity be used as a generalized characteristic of the gas-generating power of a molding sand holds true just for the stationary regime of the process.

CONCLUSIONS

1. We have analyzed the mechanism of thermal destruction of phenol-formaldehyde resin used as a binder in a mold. The kinetic parameters of the process have been determined by fitting the calculated curves to the experimental data available in the literature.

2. The mathematical model of gas release from a mold has been constructed. The model includes the heating of the molding sand by liquid metal casted into the mold, the thermodestruction of the resin, and the kinetics of secondary chemical reactions; it also includes the filtration of volatile destruction products in the mold's capillary-porous medium.

3. Experimental investigation on determination of the parameters of gas release from a mold has been carried out; the results obtained have been compared to the data of numerical modeling. It has been shown that, within the framework of the assumptions made, the mathematical model gives a fairly good description of the process in question in a wide range of variation in its parameters.

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NOTATION

A, preexponential factor in the reaction-rate constant, $(\text{cm}^3 \cdot \text{mole}^{-1})^{m-1} \cdot \text{K}^{-n} \cdot \text{sec}^{-1}$; A_k, aromatic molecule containing k aromatic rings; $A_k\bullet$ and $A_kC_2H_2\bullet$, aromatic radicals; a, relative coefficient of gas release, $\text{nm}^3/(\text{m}^2 \cdot \text{sec}^{1/2})$; c, heat capacity, J/(kg·K); E, activation energy of the reaction, J/mole; G_i, rate of yield of the ith functional group from the resin, sec^{-1}; H_{m}, crystallization heat of the metal, J/kg; h, mold-wall thickness, m; k, reaction-rate constant, $(\text{cm}^3 \cdot \text{mole}^{-1})^{m-1} \cdot \text{sec}^{-1}$; m, reaction order; N_i, mass flux of the ith gas component in the molding sand, $\text{kg}/(\text{m}^2 \cdot \text{sec})$; n, exponent of T in the reaction-rate constant; p, pressure, Pa; Q, released-gas volume, nm^3/m^2; R_i, rate of formation of the ith gas component, kg/(m^3·sec); $R = 8.31$ J/(mole·K), universal gas constant; r, average pore radius, m; T, temperature, K; t, time, sec; v, mass-mean gas velocity in the medium, m/sec; W, bulk flow of gases from the mold surface, nm^3/(m^2·sec); x, linear coordinate in the mold, m; x_i, mole fraction of the ith gas component; Y_i, concentration of the ith functional group in the resin, kg/kg of the starting resin; y_i, mass fraction of the ith gas component; α, heat-transfer coefficient, W/(m^2·K); δ, casting thickness, m; ε, emissivity of the mold surface; $\varepsilon_{\mathrm{mix}}$, porosity of the molding sand; η, gas viscosity, kg/(m·sec); φ_{mix}, mass fraction of resin in the sand; λ, thermal conductivity; W/(m·K); μ_i, molecular weight of the ith gas component, g/mole; ρ, density, kg/m^3; $\sigma = 5.67 \cdot 10^{-8}$ W/(m^2·K^4), Stefan–Boltzmann constant; ξ, thickness of the solidified metal layer, m. Subscripts: 0, initial value; a, ambient medium; i, component number; k, number of aromatic rings; m, metal; mix, molding sand (mixture).

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