NATURAL REMOVAL OF POISON GAS IMPURITIES IN OIL-SHALE MINES ATMOSPHERES

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Oil shale mine atmosphere poisoning is caused by partial absorption of poisonous gases by mine walls during various processes. It was necessary to determine the factors for mass transfer and sorption in order to calculate and regulate the self-purification process by changing the aerodynamic parameters.

Equations and calculation methods to determine the mentioned factors were compiled by way of natural experiments and mathematical modeling.

Introduction

Long-term research shows that Estonian oil-shale mines can self-purify the mine atmosphere of poison gas impurities [1]. Moreover, it is rather intensive, even though a large amount of harmful substances originating from blasting operations, exploitation of vehicles with internal-combustion engines (ICE), *etc.* pollutes the atmosphere of mine workings. The impurity concentrations in the return ventilation air are much lower than in the intakes.

The physical and chemical mechanism of poison gas absorption by the walls of mine workings, picked and transported rock, and airborne dust is based on two processes proceeding independently:

- Convective and diffusive mass transfer of the impurities dissolved in the air from the turbulent flow core to the absorption surfaces (external mass transfer)
- Mass transfer of the impurities from the air to the absorption surface (internal mass transfer)

In developed turbulent flow, mass transfer is determined by the aerodynamic characteristics of the air flow and mine workings, as well as by the physical properties of gas components. This is described by a complex system of partial differential equations – momentum equations and equations of continuity and convective diffusion.

Analytical solution of such equations is extremely complicated and is possible only in isolated special cases. Therefore it is not convenient for practical calculations. Having reliable experimental data, it is possible to use hydrodynamic theory of mass transfer based on the Reynolds analogy instead of analytical solution.

Determination of Coefficients of Mass Transfer

Coefficient of External Mass Transfer

During the movement of the gas-and-air flow in the mine workings, resistance force always occurs. Permanent transfer and exchange of the momentum between fluid layers having different velocities cause it. When turbulent core particles (molecules) get into the boundary layer their velocity u changes to u'. Having been displaced by others, these particles return into the turbulent core. Such movement is permanent.

Basing on the law of conservation of momentum, the frictional force is determined by the following formula:

$$F = Q\rho_B(u - u')$$ (1)

where Q is the gas-and-air flow per second;

ρ_B is density of a gas-and-air mixture;

u, u' are velocities of gas-and-air flow in the turbulent core and on the border of a boundary layer, respectively.

If impurity concentrations in the core and in the boundary layer are not the same, then simultaneously with transfer of mechanical energy, transfer of impurity occurs. Let c and c' denote the concentration of impurity in the core and in the boundary layer, respectively. Then the impurity amount transferred from the core to the boundary layer with turbulent flow equals

$$q = Qg\rho_B(c - c')$$ (2)

Substituting the value of $Q\rho_B$ from Equation (1) into Equation (2) gives:

$$q = \frac{Fg}{u - u'}(c - c')$$ (3)

From

$$F = \tau S_B, \quad q = q' \cdot S_B$$ (4)

where τ is tangential stress;

q' is specific flow of the impurity;

S_B is area of mine working surface

It follows that

$$q' = \frac{q}{S_B} = \frac{\tau g(c - c')}{u - u'} \tag{5}$$

As the impurity is transferred to the wall through the laminar boundary layer by mass transfer there is another way to compute q':

$$q' = \frac{D_M g\rho_B}{\delta}(c' - c_u) \tag{6}$$

In (6) D_M is coefficient of molecular diffusion;

   δ is thickness of the boundary layer;

   c_u is concentration on the wall.

Substituting $\delta = \mu \dfrac{u'}{\tau}$ into Equation (6) yields

$$q' = \frac{D_M g\rho_B}{\mu \dfrac{u'}{\tau}}(c' - c_u) = \frac{\tau g \rho_B (c' - c_u)}{\mu u \dfrac{u'}{u}} D_M \tag{7}$$

Combining Equations (5) and (7) we can easily compute

$$c - c_u = \frac{q' u}{\tau g}\left[\left(1 - \frac{u'}{u}\right) + \frac{1}{\rho_B}\mu\frac{\dfrac{u'}{u}}{D_M}\right] \tag{8}$$

which gives

$$q' = \frac{\tau(c - c_u)g}{u\left[\left(1 - \dfrac{u'}{u}\right) + \dfrac{1}{\rho_B}\cdot\dfrac{u'}{u}\cdot\dfrac{\mu}{D_M}\right]} \tag{9}$$

On the other hand, the amount of impurity absorbed by the unit of surface is proportional to the coefficient of mass transfer

$$q' = \frac{a(c - c_u)}{m} \tag{10}$$

where m is coefficient of mass transfer depending on the properties of impurities and the absorbing surface.

Calculating a from Equation (10) and taking into account Equation (8) we obtain

$$a = \frac{\tau \cdot m}{\dfrac{u}{q}\left[1 + \dfrac{u'}{u}\left(\dfrac{v}{D_M} - 1\right)\right]} \tag{11}$$

Taking into account that the relation $\dfrac{\nu}{D_m}$ represents the value of Schmidt Number (S_c), Equation (11) can be written as follows:

$$a = \frac{\tau \cdot m}{\dfrac{u}{g}\left[1 + \dfrac{u'}{u}(S_c - 1)\right]} \tag{12}$$

For the velocity at the laminar underlayer border (Blasius zone) we have

$$\frac{u'}{u} = 0.2\,\mathrm{Re}^{-0.125} \tag{13}$$

As $\tau = \beta \dfrac{u^2 \cdot g}{2}$; $\beta = 16.3\alpha$ (α is the coefficient of aerodynamic resistance

of the mine workings, $\dfrac{Nc^2}{m^4}$) [2] and $\rho_B = 1.2$ kg/m^3, we conclude

$$a = \frac{9.78\alpha mu}{1 + \dfrac{u'}{u}(S_c - 1)} \quad \text{(m/c)} \tag{14}$$

Formula (14) is universal and is applicable for any mine workings.

Since for gas mixtures $S_c \approx 1$, in that case a reduces to

$$a = 9.78\alpha mu \quad \text{(m/c)} \tag{15}$$

Equation (15) is the input equation at statement of location researches to find coefficient of convective gas exchange between impurities and mine working walls.

Coefficient of Internal Mass Transfer

Using dependence [3]

$$
c(x,t) = \frac{c_0}{2}\left\{\exp\left[-\frac{x}{2D_x}\left(u + \sqrt{u^2 + 4D_x\gamma}\right)\right]\mathrm{erf}\,c\frac{x - t\sqrt{u^2 + 4D_x\gamma}}{2\sqrt{D_x t}} - \right.
$$

$$
- \mathrm{erf}\,c\frac{x - (t-\tau)\sqrt{u^2 + 4D_x\gamma}}{2\sqrt{D_x(t-\tau)}} + \exp\left[-\frac{x}{2D_x}\left(u - \sqrt{u^2 + 4D_x\gamma}\right)\right] \times
$$

$$
\left. \times \left[\mathrm{erf}\,c\frac{x + t\sqrt{u^2 + 4D_x\gamma}}{2\sqrt{D_x(t-\tau)}} - \mathrm{erf}\,c\frac{x + (t-\tau)\sqrt{u^2 + 4D_x\gamma}}{2\sqrt{D_x(t-\tau)}}\right]\right\} \tag{16}
$$

where $c(x,t)$ is concentration of impurities;

t is time;

τ is time of impurities emission.

c_0 is initial concentration of impurities

$$\text{erf } c(\varphi) = 1 - \text{erf}(\varphi) = \frac{2}{\sqrt{\pi}} \int_0^{\varphi} e^{-\psi^2} d\psi$$

we determine the coefficient γ of internal mass transfer as follows.

Varying the value of γ in Eq. (16) and keeping x constant, we obtain a family of theoretical curves $c = c(x = \text{const}, t)$. Comparing the latter to experimentally obtained curves gives us the value of γ, in actual mine conditions. Comparison of theoretical and experimental data, along with the determination of numerical values of γ, was processed at PC EC [3].

Study of Sorption Absorption of Gaseous Impurities in the Mines of Estonian Oil Shale Basin

External Mass Transfer (Absorption by the Mine Working Surfaces)

Two processes were investigated:

A. *Absorption of carbon monoxide and nitrogen oxides that are formed during blasting operations*

B. *Absorption of nitrogen oxides and aldehydes that are evolved by ICE*

A. Experiments were carried out in a blind drift. Before sampling for carbon monoxide and nitrogen oxides (standard method [4]) after blasting charges and intermixing gases, the part of the blind drift to be measured was isolated by a brattice curtain.

B. In the isolated part (about 63-170 m) a running bulldozer engine had been moved lengthwise to produce some initial concentration of exhaust gases. Immediately after shutting the engine down, and then every 10 minutes for 5-6 hours air was sampled in five cross-sections lengthwise isolated part. In each experiment, heat and humidity parameters of the atmosphere in the mine working, and the quantity and composition of ICE exhaust gases were determined. The total number of experiments was 27. In no samples taken after 15-20 minutes from the beginning of the process were aldehydes detected in concentrations exceeding 0.002 %. Consequently, the coefficient for aldehydes mass transfer differs significantly from one. The results from statistical processing of the results of these experiments are shown in Table 1.

Table 1. Coefficients of Mass Transfer at External Absorption in Mine Workings

Series of mine experiments	Parameters of the isolated part of a mine working			Concentration of gases c, vol.%				Rate of specific adsorption W, 1/c		Coefficient of mass transfer m	
	Length L_B, m	Area of the cross section F_B, m²	Volume V_B, m³	Initial CO	Initial NO_2	Final CO	Final NO_2	CO	NO_2	CO	NO_2
1	63.8	9.9	631.6	0.040	0.1386	0.0097	0.0198	0.00087	0.00095	0.21	0.23
2	81.8	9.8	801.6	0.030	0.0524	0.0059	0.0064	0.00079	0.00091	0.19	0.22
3	91.6	9.9	897.7	0.031	0.0252	0.0056	0.0029	0.00075	0.00095	0.18	0.23
4	74.5	13.4	998.3	0.032	0.1093	0.0081	0.0152	0.00071	0.00096	0.20	0.27
5	80.0	13.2	1056	0.042	0.0964	0.008	0.0122	0.00061	0.00075	0.17	0.21
6	90.0	13.3	1197	0.024	0.1434	0.0041	0.0165	0.00078	0.00093	0.22	0.26
7	105.5	8.1	854.6	0.032	0.1213	0.0074	0.0168	0.00105	0.00109	0.23	0.24
8	99	8.1	801.6	0.048	0.1216	0.0096	0.0156	0.00087	0.00149	0.19	0.23
9	68	8.1	550.8	0.036	0.1260	0.0065	0.0145	0.00073	0.00091	0.16	0.20
10	86.1	13.1	1127.9	0.028	0.1357	0.0067	0.0194	0.0061	0.00079	0.17	0.22
11	90.0	13.1	1179	0.032	0.1319	0.0063	0.0161	0.00079	0.0009	0.22	0.25
12	95.0	13.2	1254	0.035	0.1410	0.0071	0.0183	0.00082	0.00099	0.23	0.28
13	81.5	14.8	1206.2	0.026	0.1321	0.0060	0.0183	0.00064	0.00074	0.19	0.22
14	92.5	17.5	1618.75	0.042	0.0891	0.0084	0.0111	0.00068	0.00075	0.22	0.24
15	77.6	19.8	1536.5	0.041	0.1412	0.0072	0.0162	0.00058	0.00073	0.20	0.25
16	65.2	14.9	971.5	0.048	0.1202	0.0107	0.0160	0.00077	0.00091	0.23	0.27
17	75.0	15.0	1125	0.027	0.1291	0.0054	0.0159	0.00070	0.00087	0.21	0.26
18	69.5	14.6	1014.7	0.036	0.1231	0.0062	0.0141	0.00061	0.00071	0.18	0.22

Table 1. Coefficients of Mass Transfer at External Absorption in Mine Workings (ending)

Series of mine experiments	Parameters of the isolated part of a mine working			Concentration of gases c, vol%				Rate of specific adsorption W, 1/c		Coefficient of mass transfer m	
	Length L_B, m	Area of the cross section F_B, m^2	Volume V_B, m^3	Initial CO	Initial NO$_2$	Final CO	Final NO$_2$	CO	NO$_2$	CO	NO$_2$
19	82.0	19.5	1599	0.030	0.0431	0.0067	0.0054	–	0.00073	–	0.25
20	83.6	17.4	1454.6	0.026	0.1351	0.0049	0.0190	–	0.00073	–	0.23
21	170.6	17.5	2985.6	0.041	0.1300	0.0072	0.0153	–	0.00074	–	0.24
22	145.5	17.4	2531.7	0.022	0.1312	0.0051	0.175	–	0.00084	–	0.27
23	110.0	14.8	1628	0.028	0.1323	0.0055	0.0181	–	0.00088	–	0.26
24	121.4	14.6	1772.4	0.032	0.1193	0.0057	0.0136	–	0.00095	–	0.28
25	117.6	14.6	1716.9	0.019	0.1447	0.0044	0.0196	–	0.00075	–	0.22
26	142.2	14.8	2076.1	0.021	0.1311	0.0041	0.0156	–	0.00072	–	0.21
27	109.4	14.8	1619.1	0.017	0.0963	0.0029	0.0112	–	0.00074	–	0.22

Internal Mass Transfer (Absorption in the Flow Space)

In this case, absorption of exhaust and explosive gases in open mine workings and in blind drifts was investigated. To study the absorption of exhaust gases, a vehicle with an ICE (a bulldozer) operating at a constant mode for a predetermined period was placed in open mine workings at a distance of 30 m from a chamber block. The air samples were taken at the ICE exhaust pipe exit and in the mine workings cross-sections (x = const) at various distances (up to 350 m) from the vehicle. Distance measurements were lengthwise along the path of the ventilation stream.

Temperature, quantity and relative humidity of the air passing along the mine working were measured. If necessary, the amount of air was adjusted by a brattice curtain.

Air samples for determining carbon monoxide and nitrogen oxides formed after blasting operations were taken in a blend drift outside the active intermixing zone (95-120 m from the face).

Based on experimental data, curves of impurity concentration changes $\tilde{c} = \tilde{c}(x = const, t)$ with external and internal mass transfer were plotted. Concentration curves, resulting from internal mass transfer only, were obtained from the curves $\tilde{c} = \tilde{c}(x = const, t)$. This was accomplished by adding the value of concentration of impurities to their ordinates, as caused by the external mass transfer, which is determined according to following equation:

$$c = c\frac{2c_0}{B}\exp\left(\frac{ux}{2D_x}\right)\sum_n \cos\lambda_n y\left(\cos\frac{\lambda_n B}{2} - 1\right)\times$$

$$\times\left\{\exp\left[-\sqrt{\frac{1}{D_x}\left(\frac{u^2}{4} + \lambda^2 D_y + \gamma\right)}\right]\cdot x\cdot\mathrm{erf}\,c\left[\frac{x}{2\sqrt{D_x t}} - \sqrt{\left(\frac{u^2}{4} + \lambda^2 D_y + \gamma\right)t}\right] + \right.$$

$$+\exp\left[\sqrt{\frac{1}{D_x}\left(\frac{u^2}{4} + \lambda^2 D_y + \gamma\right)}\cdot x\right]\times\mathrm{erf}\,c\left[\frac{x}{2\sqrt{D_x t}} + \sqrt{\left(\frac{u^2}{4} + \lambda^2 D_y + \gamma\right)t}\right] -$$

$$-\sigma_0(t-\tau)\left[\exp\left(-\sqrt{\frac{1}{D_x}\left(\frac{u^2}{u} + \lambda^2 D_y + \gamma\right)}x\right)\times\right.$$

$$\times\mathrm{erf}\,c\left[\frac{x}{2\sqrt{D_x(t-\tau)}} - \sqrt{\left(\frac{u^2}{4} + \lambda^2 D_y + \gamma\right)(t-\tau)}\right] + \exp\left[\sqrt{\frac{1}{D_x}\left(\frac{u^2}{4} + \lambda^2 D_y + \gamma\right)}\cdot x\right]\times$$

$$\left.\left.\times\mathrm{erf}\,c\left[\frac{x}{2\sqrt{D_x(t-\tau)}} + \sqrt{\left(\frac{u^2}{4} + \lambda^2 D_y + \gamma\right)(t-\tau)}\right]\right\}\right. \tag{17}$$

at $\gamma = 0$; $a \neq 0$

Here B is the width of mine workings; λ_n is characteristic values

$$\sigma_0(t) = \begin{cases} 1, t > 0 \\ 0, t \leq 0 \end{cases} \text{ is a unit step function}$$

Coefficient a is determined by the Formula (15). The curves of concentration change $c_{int} = c(x = \text{const}, t)$ obtained this way were compared to the family of curves $c = c(x = \text{const}, t)$ obtained by solution of Equation (16) with various γ values. As a result, values of internal absorption coefficients were obtained.

Analysis of theoretical and experimental works has shown that coefficient of internal mass transfer depends on the following quantities:

$$\gamma = f(u, \sqrt{F_B}, v, D_x) \tag{18}$$

After solution of the functional dependence (18) we obtain

$$\frac{\gamma \sqrt{F_B}}{D_x} = k(\frac{u\sqrt{F_B}}{v})^\beta \cdot (\frac{v}{D_x})^\sigma \tag{19}$$

To obtain a formula for calculating coefficient γ, let us represent Equation (19) in logarithmic form:

$$(\ln \frac{\gamma\sqrt{F_B}}{D_x} \bigg| \ln \frac{u\sqrt{F_B}}{v})$$

Let us open it using experimental data from Equation (19). Corresponding values of the parameters of Equation (19) are presented in Table 2.

Table 2. **Data for Determination of the Coefficient of Internal Absorption of Impurities**

F_B, m^2	u, m/c	D_x, m^2/c	$\ln\gamma\dfrac{\sqrt{F_B}}{D_x}$	$\ln\dfrac{u\sqrt{F_B}}{v}$	$\ln\dfrac{v}{D_x}$
15.5	1.03	15.15	-7.968	12.528	-13.846
16.8	0.42	6.23	-7.161	11.671	-12.957
18.3	1.49	16.65	-8.099	12.980	-13.940
15.7	1.94	24.24	-8.441	13.167	-14.316
20.3	0.56	8.99	-7.416	12.053	-13.324
17.5	0.58	7.73	-7.321	12.014	-13.173
15.1	0.38	5.56	-7.066	11.517	-12.843
16.8	1.04	13.41	-7.879	12.578	-13.724
18.1	0.27	5.25	-6.922	11.997	-13.344
15.3	0.61	9.17	-7.563	11.449	-12.865
19.8	0.31	5.68	-6.969	11.449	-12.865
14.8	0.29	4.39	-6.893	11.237	-12.607

Processing the data given in Table 2 revealed the following formula for determination of γ:

$$\gamma = 5.886 \frac{D_x}{\sqrt{F_B}} \text{Re}^{-0.769} \tag{20}$$

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