Methodological foundations for the system analysis principles application for modeling the phenomena of heat transfer in the technological cleaning process of tanks for oil products.

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Abstract. The article is devoted to the determination of the methodological foundations for the application of the system analysis principles for modeling the phenomena of heat transfer in the technological cleaning process of tanks for oil products. The article deals with the spontaneous combustion problem of pyrophoric deposits in oil and gas industry and a method for solving it using the principles of system analysis. The process of spontaneous combustion of pyrophoric deposits has several stages, therefore, decomposition of this process and further analysis of its structure are relevant. On the basis of a system analysis, the process stages of the pyrophoric deposits’ spontaneous combustion have been determined and general and specific tasks have been formulated.

1. Introduction
Vertical steel tanks for storage of oil and oil products are potentially dangerous objects due to the circulation of flammable substances in them. In addition to the main causes of a fire, such as the presence of an open flame, the manifestation of atmospheric and static electricity, etc., this system has another potential hazard - spontaneous combustion of pyrophoric deposits - substances capable of spontaneous combustion in contact with atmospheric oxygen. Pyrophoric deposits consist of sulfides, polysulfides, oxides, iron hydroxides, elemental sulfur, its oxides, and heat formation occurs from the sulfides oxidation, the danger lies in the complex action of the components. In the article [1], the oxidation process of iron sulfides is divided into three stages: at the first stage, electrochemical reactions predominate, due to the presence of water. Presumptive reactions at this stage are [2, 3]:

$$FeS_2 + O_2 \rightarrow FeS + SO_2 + 222.5 \text{ kJ}$$

$$2FeS_2 + 7.5O_2 + H_2O \rightarrow Fe_3(SO_4) + H_2SO_4 + 2777 \text{ kJ}$$

Further, in the second stage, upon reaching 70-80°C an increase in temperature is reduced presumably due to an increase in the water evaporation intensity and a decrease in electrochemical reactions. The influence of water on this stage still needs to be checked. The third stage starts with temperature 100-110°C, where chemical reactions start prevailing. The first and third stages are
characterized by a rather rapid rise in temperature, at the second stage even a slight decrease in temperature is observed.

Iron sulfides by themselves, when interacting with air, can heat up to a temperature 600-700 °C, however, it was shown in [4] that ignition occurs already at a temperature 200-210 °C, which corresponds to the self-ignition temperature of sulfur vapor. According to the article [5], spontaneous combustion of pyrophoric deposits was an ignition source in 12.8% of cases of fires on tanks. Most often, fires from spontaneous combustion of pyrophoric deposits occur during daylight hours, in sunny weather, in the presence of through holes in the tank, during the tank’s long-term operation without cleaning, as well as when pumping oil [6]. Therefore, the consideration of heat transfer processes in the reservoir is an urgent task.

2. System analysis of the pyrophoric deposits’ heating process

2.1. Building a hierarchical structure
When considering the problem of modeling the phenomena of heat transfer in the process of technological cleaning of reservoirs for oil products when heating pyrophoric deposits, it is necessary to use the system analysis methods. The system analysis strategy implies building a hierarchical structure of the process [7, 8] - breaking the problem into the levels, where the chemical reaction kinetics will be the lower level. The second level will be a chemical reaction in a layer of pyrophoric deposits, the third level will be heat transfer throughout the entire thickness from the air outside to the air inside the tank.

The whole process of heating a layer of pyrophoric deposits can be described by a generalized schematic-graphic model in the form of a structural diagram (Figure 1), where the input data will be:
- thickness of outer paint layer, steel tank wall, pyrophoric deposits (δP, δST, δD respectively);
- heat capacity, density, thermal conductivity of the above layers (c, ρ, λ respectively);
- perturbation:
  - heat flux from solar radiation qs;
  - heat generated by oxidation of pyrophoric deposits qD;
output data:
- temperature distribution T(x, τ) in time by thickness x.

![Figure 1. Block diagram of the object](image)

At the heat transfer level, the problem of modeling heat transfer in the layer of pyrophoric deposits is formulated.

2.2. Physical model description
To formulate a mathematical problem, it is necessary to describe a physical model. As mentioned above, most often spontaneous combustion of pyrophoric deposits occurs in sunny weather, therefore, it is necessary to take into account the sun radiation effect in the model. The very wall of the reservoir with pyrophoric deposits can be considered as a one-dimensional three-layer endless plate (Figure 2), since the outer part of the tank, as a rule, is covered with a light paint for thermal insulation, and pyrophoric deposits are formed on the inside due to interaction with hydrogen sulfide. For simplicity, it is assumed that pyrophoric deposits have a homogeneous structure throughout the entire thickness.
Figure 2. Illustration of a model for heating a tank wall by solar radiation 
and oxidation of pyrophoric deposits

c, ρ, λ – heat capacity, density, thermal conductivity, respectively,
1, 2, 3 – indices of paint layers, steel wall and pyrophoric deposits, respectively;
q_S – heat flux from solar radiation; q_D – heat generated by oxidation of pyrophoric deposits; T_E –
environment temperature and the temperature inside the tank;
x – coordinate; T – temperature

2.3. A mathematical problem
Let us formulate a mathematical problem and define the boundary conditions. Heat propagation in the 
plate will be carried out according to the differential heat conduction equation:

\[ \frac{\partial T_1(x, \tau)}{\partial \tau} = \frac{a_1}{\lambda_1} \frac{\partial^2 T_1(x, \tau)}{\partial x^2} \quad (\tau > 0; \quad 0 \leq x \leq \delta_p); \]  
(1)

\[ \frac{\partial T_2(x)}{\partial \tau} = \frac{a_2}{\lambda_2} \frac{\partial^2 T_2(x)}{\partial x^2} \quad (\tau > 0; \quad \delta_p \leq x \leq \delta_{ST}); \]  
(2)

\[ \frac{\partial T_3(x, \tau)}{\partial \tau} = \frac{a_3}{\lambda_3} \frac{\partial^2 T_3(x, \tau)}{\partial x^2} + \frac{q_D}{c_3 \rho_3} + \frac{\varepsilon \rho_q}{C_q} \frac{\partial u(x, \tau)}{\partial \tau} \quad (\tau > 0; \quad \delta_{ST} \leq x \leq \delta_D); \]  
(3)

where: \( a \) – is a thermal diffusivity;
\( \varepsilon \) – is a phase transition criterion;
\( \rho_q \) – denotes the specific heat of vaporization;
u – is a moisture content.

Initial conditions:

\[ T_1(x, \tau)|_{\tau=0} = T_{10}(x), \]  
(4)

\[ T_2(x, \tau)|_{\tau=0} = T_{20}(x), \]  
(5)

\[ T_3(x, \tau)|_{\tau=0} = T_{30}(x). \]  
(6)

Border conditions:
on the left border
\[
q_S = \frac{\partial T_1(x, \tau)}{\partial x} \quad (x = 0),
\]

on the right border
\[
\alpha_3 [T_E - T_3(x, \tau)] - (1 - \varepsilon) \rho_q \rho_0 [u(x, \tau) - u_E] = \lambda_3 \frac{\partial T_1(x, \tau)}{\partial x} \quad (x = \delta_D);
\]

where: \( \rho_0 \) – is medium density;
\( u \) – is transfer potential;
\( u_E \) – is a substance potential at the interface of pyrophoric deposits with the environment.

at the contact point between the layers 1 and 2
\[
\lambda_1 \frac{\partial T_1(\delta_p, \tau)}{\partial x} = \lambda_2 \frac{\partial T_2(\delta_p, \tau)}{\partial x},
\]

\[
T_1(\delta_p, \tau) = T_2(\delta_p, \tau);
\]

at the contact point between the layers 2 and 3
\[
\lambda_2 \frac{\partial T_2(\delta_{ST}, \tau)}{\partial x} = \lambda_3 \frac{\partial T_3(\delta_{ST}, \tau)}{\partial x},
\]

\[
T_2(\delta_{ST}, \tau) = T_3(\delta_{ST}, \tau).
\]

The formulated mathematical problem (1) - (12) is a complex system and it is necessary to use such a method of system analysis as decomposition, to break a complex system into the subsystems for its solution.

2.4. Decomposition of a mathematical problem as a system

The solution of the mathematical problem (1) - (12) will be carried out numerically and analytically after it is divided into the subsystems as follows: we will simultaneously consider the effect of the heat flow from the sun \( q_S \) and the heat generation from an internal source during the pyrophoric deposits’ oxidation \( q_D \).

The decomposition of the problem (1) - (12) for the subsequent solution on the heat flux effect from the sun on the left boundary is shown in Figure 3 (the conditions (13) - (16)), according to the generation of heat from an internal source during the pyrophoric deposits’ oxidation in the layer in Figure 4 (the conditions (17) – (20)).

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**Figure 3.** Illustration of a model of heating the outer paint layer of a tank by solar radiation and temperature profiles at different time values (at \( \tau < \tau_{i+1} \))

\[
\frac{\partial T_1(x)}{\partial \tau} = a_1 \frac{\partial^2 T_1(x)}{\partial x^2} \quad (\tau > 0; \quad 0 \leq x \leq \delta_p),
\]

(13)
Initial conditions:
\[ T_i(x, \tau) \big|_{\tau=0} = T_{10}(x). \] (14)

Border conditions:
on the left border
\[ q_s = \lambda_i \frac{\partial T_i(x, \tau)}{\partial x} \quad (x = 0), \] (15)
on the right border
\[ \lambda_i \frac{\partial T_i(x, \tau)}{\partial x} = 0 \quad (x = \delta_p); \] (16)

\[ \begin{array}{c}
\delta_{ST} \\
\alpha_3 \quad \rho \quad \lambda_3
\end{array} \]
\[ \delta_D \]
\[ x \]

\[ T \]

\[ q_0 \]
\[ T_E \]

\[ \tau \]

\[ \frac{a_3}{\delta_{ST}} \leq x \leq \delta_D \]

\[ \frac{\partial T_3(x, \tau)}{\partial \tau} = a_3 \frac{\partial^2 T_3(x, \tau)}{\partial x^2} \quad (\tau > 0; \quad \delta_{ST} \leq x \leq \delta_D), \] (17)

\[ T_3(x, \tau) \big|_{\tau=0} = T_{10}(x). \] (18)

\[ \lambda_3 \frac{\partial T_3(x, \tau)}{\partial x} = 0 \quad (x = \delta_{ST}); \] (19)

\[ a_3 \left[ T_E - T_3(x, \tau) \right] = \lambda_3 \frac{\partial T_3(x, \tau)}{\partial x} \quad (x = \delta_D); \] (20)

2.5. Methodology for solving the problem.
The subsystems obtained in Section 2.4 will be solved sequentially at small values of time until the temperature profile of the other layers’ boundaries is reached. When the temperature profile reaches the boundary of another layer, a temperature gradient arises and a boundary condition of the second kind appears in the problem (which corresponds to the conditions (9), (10) of the general problem).

Let us consider the case when the temperature inside the tank is kept constant, and outside it rises due to heating by solar radiation. Then the temperature fields (Figure 5) will be characterized by the curves for \( \tau_1, \tau_2, \tau_3 \).
Figure 5. Illustration of temperature profiles at different time values $\tau$

When $\tau = \tau^*$ the temperature profile reaches the border $\delta_P$. Prior to this, the temperature field varied along the curves for $\tau_1$, $\tau_2$. In this case, the problem was determined by the equation (13) with the initial condition (14) and the boundary conditions (15)-(16).

From the moment in time $\tau_3$ the calculation system includes zone 2 - the steel wall of the tank. At a point with a coordinate $x = \delta_P$ the heat conduction equation will be replaced in the form of expression (2). The initial condition for the first step of calculating the temperature field is the equation (5). The boundary condition on the left boundary is the condition of heat transfer at the contact point of the layers between the layers 1 and 2 (9), taking into account the achieved temperature profile (21):

$$- \lambda_1 \frac{\partial T_1(\delta_P, \tau_3)}{\partial x} = q_1(\tau_3) = \lambda_2 \frac{\partial T_2(\delta_P, \tau_3)}{\partial x}$$

(Boundary conditions on the right border $x = \delta_{ST}$):

$$- \lambda_2 \frac{\partial T_2(\delta_{ST}, \tau_3)}{\partial x} = 0$$

Changing the temperature fields at a time step $\tau_4$ will have the form of curves at $\tau_4$, $\tau_5$, $\tau_6$. From the moment in time $\tau_6$ the layer 3 is additionally switched on - pyrophoric deposits and the calculation is carried out in the same way as for the layer 2.

When considering the case of the internal heat source $q_{ID}$ appearance in the layer 3, the calculation will be performed from the left and right boundaries. The temperature profile from the left border will look the same as when considering the case of heating the left border by solar radiation. As there will be an internal heat source in the layer 3, then heat will spread towards the left boundary.

The analytical solution of the system of equations (13) - (16) for a similar case is presented in the work [7] (23):

$$\Theta(\bar{x}, F_0) = \frac{T_1(x, \tau) - T_e}{T_e} = K_i \left\{ (1 - \bar{x}) + 2 \sum_{n=1}^{\infty} \left[ \left( -1 \right)^n \sin \left[ \mu_n \left( 1 - \bar{x} \right) \right] \exp \left( -\mu_n^2 F_0 \right) \right] \right\} +$$

$$+ 2 \sum_{n=1}^{\infty} \cos \left[ \frac{\mu_n \bar{x}}{\mu_n^2} \right] \exp \left( -\mu_n^2 F_0 \right) \left( -1 \right)^n \frac{1}{\mu_n^2} \int_0^{F_0} T_0(\xi) \cos(\mu_n \xi) d\xi,$$

where the following notation is introduced in a dimensionless form (24):
\[
\Theta(\bar{x}, Fo) = \frac{T_I(x, \tau) - T_E}{T_E}; \quad F_o = \frac{q_I}{\delta_p^2}; \quad \bar{x} = \frac{x}{\delta_p}; \quad Ki = \frac{q_I}{\lambda E T_E} \sqrt{\frac{\delta_p}{\tau}} \quad (24)
\]

\(\mu_n\) – denotes the characteristic equation roots and can be defined as: \(\mu_n = n \cdot \pi\).  

\(Ki\) – is a Kirpichev criterion;  
\(\bar{x}\) – denotes the relative coordinate;  
\(F_o\) – is a Fourier test;  
\(\Theta(\bar{x}, Fo)\) – is dimensionless temperature as a function of relative coordinate and Fourier number.

**Summary**  
The analysis results show that to determine the temperature distribution in the vertical tank wall thickness and pyrophoric deposits, it is necessary to split the general problem into the smaller ones.

As a result of the work performed, it is possible to assume:  
- homogeneous layers, which will be used for the calculation have been defined;  
- a method for calculating temperatures by a numerical-analytical method (by sequentially determining the temperature profiles along the layer thickness) has been proposed;  
- the analytical solution for the sequential calculation of the temperature profile over the layers thickness has been determined. The resulting equation gives a possibility to obtain the temperature profiles (as shown in Figure 5) at the stage of heating three layers by the sun’s rays. When an internal heat source occurs in the layer 3, the temperature profile will be different. The subject of further research is to obtain the temperature profiles taking into account the occurrence of an internal heat source in the pyrophoric deposits’ layer.

**References**

[1] Dou Z, Jiang J C, Zhao S P, Mao G B, Zhang M G, Wang L, Wang Z R 2015 Experimental investigation on oxidation of sulfurized rust in oil tank *Journal of Loss Prevention in the Process Industries* **38** 156-162. DOI: https://doi.org/10.1016/j.jlp.2015.09.009.

[2] Beilin Yu A, Niselson L A, Begishev I R, Filimonov L I, Shishkanov B A, Ashcheulova I I, Podobaev A N, Reformatorskaya I I 2007 Corrosive pyrophoric deposits as promoters of spontaneous combustion of reservoirs with sulfurous oil *Journal of Metals Protection* **43** (3) 290-295.

[3] Boyarov A N, Sumarchenko I A 2009 Ensuring safety in the operation of oil and oil products storage tank farms *Youth and Science: Reality and the Future. Materials of the II Int. scientific-practical. conf. March 3, 2009 – Nevinnomyssk, VIII: Natural and applied sciences* 565-566.

[4] Boyarov A N, Karamyshev V G 2008 Investigation of the pyrophoric deposits behavior when heated under various conditions *STJ Interval* **9** 37-41.

[5] Petrova N V, Cheshko I D, Galishev M A 2016 Analysis of the practice of expert research of fires at oil and oil products storage facilities *Journal "Bulletin of the St. Petersburg University of the State Fire Service of the Ministry of Emergency Situations of Russia"* **3**. Information on http://vestnik.igps.ru/wp-content/uploads/V83/ 7.pdf

[6] Volkov O M 1984 *Fire safety of tanks with oil products* (Moscow, Nedra) 151.

[7] Kafarov V V, Dorokhov I N 1976 *System analysis of chemical technology processes. Basics of strategy* (Moscow, Nauka) 500.

[8] Natareev S V 2007 *System Analysis and Mathematical Modeling of Chemical Technological Processes Ivanovo state chemical-technological university: study guide Ivanovo* 80.

[9] Fedosov S V, Aloyan R M, Ibragimov A M, Gnedina L Yu, Aksakovskaya L N 2005 *Freezing of wet soils, basements and foundations* (Moscow, ASV Publishing House) 277.