On the modelling of the extraction process of rare metals from metal-containing systems by the method of filtration combustion

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Abstract. Numerical modelling of heterogeneous combustion in porous media with phase transitions is considered. To describe the propagation of time-dependent one-dimensional waves of heterogeneous combustion of metal-containing mixtures, a mathematical model and a numerical method are proposed. The model is based on the assumption of interacting interpenetrating continua using classical approaches of the theory of filtration combustion and includes equations of state, continuity, momentum conservation and energy for each phase. The numerical method is based on a combination of explicit and implicit finite difference schemes. The carried out numerical calculations showed the efficiency of the proposed model and allowed one to detect the concentration of the condensed metal near the front of the combustion wave.

1. Introduction

In recent decades, the use of so-called rare metals in various fields of engineering keeps growing with the ever-increasing scale. In this group there are various metals which are used in relatively small quantities in modern production. The scale of production, the range of products, the state of technology and the field of application of rare metals have not yet stabilized and continue to grow rapidly. The constant expansion of the scope of their application provides savings of natural resources, improves product quality, reduces energy and material costs. Advanced modern industry is impossible without rare elements: germanium, indium, tantalum are used for the element base of optics and microelectronics; gallium and scandium are used for the most powerful lasers; neodymium, samarium, dysprosium are used for a new class of permanent magnets; yttrium, lanthanum, strontium, bismuth, thallium are used for actively developed high-temperature superconductors; zirconium, yttrium are used for new structural ceramics; niobium, lithium, vanadium, beryllium, rhenium, scandium are used as aviation and space materials; zirconium, hafnium are used for atomic technology; lithium, beryllium, vanadium are used for thermonuclear energy. Thus, the demand for rare metals, which are necessary for the innovative development of industrialized countries, will remain stable in the long run, and the need for them increases annually [1].

The largest consumers of rare metals are the countries that have achieved the greatest success in scientific and technical progress: the USA, the countries of Western Europe and Japan. At the same
time, the list of countries producing rare metals is very short, and China takes the first place for production and export and has about 50% of world reserves of rare metals. Taking into account the policy of the Chinese government, the shortage of rare metals is a world problem [2], the solution of which could be the development of its own base of mineral resource or, if the own base is absent, the search for new sources of raw materials. The unconventional sources of rare metals are oil and coal. For example, over 60 chemical elements have been discovered in oils, most of which are rare metals. Vanadium, nickel, gold, molybdenum, uranium and some other metals are extracted from petroleum and bitumen on an industrial scale in the USA, Canada, Peru, Venezuela, Mexico and some other countries.

Thus, stocks of rare and valuable metals in heavy oils, bitumen and coals are important as a potential source for their industrial production. Also it should be noted, that petroleum coke, produced in large quantities in the oil refining, is often a more valuable raw material for the industrial production of rare and valuable metals than ore.

Currently, research is being conducted to find environmentally friendly and efficient processes for the extraction of valuable and rare metals [3]. The main difficulty in the extraction of metals is that, as a rule, their concentration in the raw material is much less than a percent. In the paper [4] the possibility of selective concentration of molybdenum in a filtration combustion wave is shown when its initial concentration in raw material is equal to 0.15% by weight. The superadiabatic regimes of filtration combustion are characterized by high energy efficiency and stability to changes in the composition of the fuel due to intensive internal heat exchange processes, which allows accumulation of thermal energy on the combustion front [5]. A high temperature region with intensive processes of interfacial heat and mass transfer during countercurrent phases can lead to the formation of a zone structure. In each zone, physicochemical processes take place, which are determined by the conditions in this zone (temperature, phase properties, concentrations of reagents, etc.). Spatial separation of zones provides localization of certain substances in certain zones in accordance with their physicochemical properties [6]. As a result, the filtration combustion can be very useful for extracting some metals, especially those that can form relatively volatile products (both oxidation and reduction products), because even when their equilibrium content in the gas phase is low, in a gas stream they are transported together with the gas phase, shifting chemical equilibrium in the right direction. Both some free metals (for example, zinc, cadmium, mercury, arsenic, selenium, tellurium, tantalum) and their oxidized forms (for example, molybdenum and rhenium trioxides, arsenic, selenium, tellurium and tantalum oxides) can be transferred during such processes. Since mass transfer of volatile substances from the reaction mixture is accompanied by constant evaporation and condensation processes, in the case of mass transfer of several products from the initial mixture, they can be spatially separated depending on their volatility, adsorption coefficients, etc. It becomes possible to create efficient technologies for extracting the valuable components from poor ores or from waste, dumps, etc.

In the present work a novel mathematical model and a numerical method are proposed for describing the time-dependent one-dimensional waves of filtration combustion of metal-containing mixtures.

2. Mathematical model and numerical method

Consider a motionless porous object with a height $H$, which is bounded by impermeable non-heat-conducting side walls and opened on bottom and top. Suppose that a cold gas can flow into the porous object through its bottom due to forced filtration; the gas can flow through a porous medium and flow out through object top. Assume that a solid porous substance consists of combustible component (or fuel) and inert component including metal-containing substance. The gas phase can include oxidizer (oxygen) and evaporated metal. The solid combustible material transforms into gaseous products in the reaction with gaseous oxidizer, so we have the following expression:

$$\text{Solid fuel} + (\mu_g)\text{Oxidizer} \rightarrow (1+\mu_g)\text{Gaseous product}, \tag{1}$$
where $\mu_g$ is the mass stoichiometric coefficient for oxidizer.

Only the solid combustible component and the oxidizer from the gas phase (oxygen) can react chemically. The metal-containing substance is inert, does not react chemically and undergoes two phase transitions: when it is heated, it can melt (heat is consumed) and then evaporates to gaseous products (heat is consumed), which can condense when gas phase is cooled (heat is generated). The liquid phase of the metal remains motionless and is bounded up with the solid (due to capillary effects); when the liquid phase is cooled, it solidifies (heat is generated). Suppose that the processes of metal melting and solidification occur at fixed temperature $T_{melt}$, and the processes of metal evaporation and condensation occur at fixed temperature $T_{evap}$.

Introduce the following notation: $\partial \rho_{cm} / \partial t$ is the rate of changing the effective density of the condensed metal due to evaporation, or (on average) the rate of changing the mass of the condensed metal per unit volume due to evaporation; $\partial \rho_{gm} / \partial t$ is the rate of changing the effective density of the evaporated metal due to condensation, or (on average) the rate of changing the mass of the evaporated metal per unit volume due to condensation. The mathematical model is based on the assumption of interacting interpenetrating continua [7] using classical approaches of the theory of filtration combustion [8] and includes the following equations:

energy for solid phase:

$$\left(\rho_{cf}c_{cf} + \rho_{ci}c_{ci} + \rho_{cm}c_{cm}\right) \frac{\partial T_c}{\partial t} = -a_0(T_c - T_g) + \rho_{cf} \rho_{comb} W + (1 - a_g) \lambda_c \Delta T_c - \rho_{cm} Q_{melt} \frac{\partial F}{\partial t} - Q_{evap} \frac{\partial \rho'_{cm}}{\partial t},$$  (2)

energy for gas:

$$\rho_g c_g \left( \frac{\partial T_g}{\partial t} + (v_g \cdot \nabla)T_g \right) = a(T_c - T_g) + a_g \lambda_g \Delta T_g + Q_{evap} \frac{\partial \rho'_{gm}}{\partial t},$$  (3)

continuity and state for gas:

$$\frac{\partial \rho_g}{\partial t} + \nabla \cdot (\rho_g v_g) = \rho_{cf} W + \frac{\partial \rho'_{cm}}{\partial t} - \frac{\partial \rho'_{gm}}{\partial t}, \quad p = \frac{\rho_g RT_g}{a_g M},$$  (4)

momentum conservation for gas:

$$\rho_g \left( 1 + \chi(1 - a_g) \right) \frac{\partial v_g}{\partial t} + (v_g \cdot \nabla)v_g = -a_g \nabla p + \rho_g v_g - a_g^2 \frac{\mu}{k_1} v_g - \left[ \rho_{cf} W + \frac{\partial \rho'_{cm}}{\partial t} - \frac{\partial \rho'_{gm}}{\partial t} \right] v_g, \quad (5)$$

oxidizer concentration:

$$\rho_g \left( \frac{\partial C}{\partial t} + (v_g \cdot \nabla)C \right) = \nabla \cdot \left( \rho_g D_g \nabla C \right) - \mu_g \rho_{cf} W - \left[ \rho_{cf} W + \frac{\partial \rho'_{cm}}{\partial t} - \frac{\partial \rho'_{gm}}{\partial t} \right] C, \quad (6)$$

chemical kinetics:

$$W = (1 - \eta) C k \exp\left(- E / (R T_c)\right), \quad \frac{\partial \eta}{\partial t} = W, \quad (7)$$
mass conservation for evaporated metal in gas:

\[ \frac{\partial \rho_{gm}}{\partial t} + \nabla \cdot (\rho_{gm} \mathbf{v}) = \frac{\partial \rho'_{gm}}{\partial t} + \frac{\partial \rho'_{cm}}{\partial t}, \quad (8) \]

mass conservation for components of condensed phase:

\[ \frac{\partial \rho_{cm}}{\partial t} = -\frac{\partial \rho'_{cm}}{\partial t} + \frac{\partial \rho'_{gm}}{\partial t}, \quad \rho_{cf} = (1 - \eta)\rho_{cf0}, \quad (9) \]

porosity:

\[ a_g = a_g0 + a_{cf0}\eta + \frac{\rho_{cm0} - \rho_{cm}}{\rho_{cm0}}a_{cm0}. \quad (10) \]

oxidizer diffusion and gas viscosity:

\[ D_g = D_g0 \left( \frac{T_g}{273} \right)^{b}, \quad \mu = \frac{c_{s1}T_0^{1.5}}{c_{s2} + T_g}. \quad (11) \]

Here \( a \) is the volume concentration, \( b \) is the exponent in the expression for diffusion coefficient, \( C \) is the mass concentration of oxidizer, \( c \) is the specific heat capacity, \( c_{s1} \) and \( c_{s2} \) are the constants in Sutherland’s formula, \( D_g \) is the diffusion coefficient of gas, \( E \) is the activation energy, \( F \) is the liquid fraction in condensed metal, \( g \) is the gravity acceleration, \( k \) is the pre-exponential factor in the expression for the rate of reaction, \( k_1 \) is the permeability coefficient, \( M \) is the molar mass of gas, \( p \) is the gas pressure, \( Q \) is the heat release of reaction, \( R \) is the universal gas constant, \( t \) is the time, \( T \) is the temperature, \( \mathbf{v}_g \) is the gas velocity, \( W \) is the rate of chemical reaction, \( \alpha \) is the constant determining the interphase heat transfer intensity, \( \eta \) is the degree of conversion of the combustible component of solid medium, \( \lambda \) is the thermal conductivity (including radiation heat transfer according to diffusion approximation), \( \mu \) is the dynamic viscosity of gas, \( \rho \) is the effective (or bulk) density (i.e., the product of phase density and volumetric concentration), \( \chi \) is the coefficient, taking into account the inertial interaction of the phases in their relative motion \([7]\), \( \nabla \) is the del (nabla) operator, and \( \Delta \) is the Laplace operator; subscripts: "0" denotes the initial moment, "\( c \)" denotes the condensed phase, "comb" denotes the combustion, "evap" denotes the evaporation, "\( f \)" denotes the combustible component (fuel), "\( g \)" denotes the gas, "\( i \)" denotes the inert component, "\( m \)" denotes the metal substance, "\( melt \)" denotes the melting.

The boundary conditions for system (2)-(11) are following. At the bottom of the porous object (at the open boundary where gas flows into the object) gas temperature, mass concentration for the oxidizer and density of metal in gas are known. Also, at this boundary we specify the gas pressure or gas velocity. At the object top (the open boundary where gas flows out of the porous object to an atmosphere) the pressure and conditions for gas temperature, oxidizer concentration and density of metal in gas are known. The conditions of heat exchange at the top and bottom of the porous object and on the bounding impermeable walls are also known. Thus, the boundary conditions for system of equations (2)-(11) can be writing in the following form:

\[ p\big|_{x \in G_i} = p_0(x) \text{ or } \mathbf{v}_g\big|_{x \in G_i} = \mathbf{v}_g0(x), \quad T_g\big|_{x \in G_i} = T_g0, \quad C\big|_{x \in G_i} = C_0 \text{ and } \rho_{gm}\big|_{x \in G_i} = 0, \quad \text{if } \mathbf{v}_g\big|_{x \in G_i} \cdot \mathbf{n}\big|_{x \in G_i} \leq 0, \quad (12) \]
\[ p|_{x \in G_1} = p_0(x), \ \partial T_g / \partial n|_{x \in G_1} = 0, \ \partial C / \partial n|_{x \in G_1} = 0 \text{ and } \partial \rho_{gm} / \partial n|_{x \in G_1} = 0, \]

\[ \text{if } v_g|_{x \in G_1} \cdot n|_{x \in G_1} > 0, \] (13)

\[ \lambda_c \partial T_c / \partial n|_{x \in G_1} = \beta \left( T_g - T_c|_{x \in G_1} \right), \ \partial T_c / \partial n|_{x \in G_2} = 0, \] (14)

\[ \partial T_g / \partial n|_{x \in G_2} = 0, \ \ v_g|_{x \in G_2} \cdot n|_{x \in G_2} = 0, \] (15)

where \( G_1 \) is the object boundary opened to the atmosphere, \( G_2 \) is the impermeable boundary of the object, \( n \) is the outward vector directed normally to \( G_1 \) or to \( G_2 \), \( \beta \) is the heat removal coefficient.

For investigating the time-dependent waves of heterogeneous combustion of metal-containing mixtures in one-dimensional case a numerical method has been developed. It should be noted, that the proposed mathematical model is similar to the model for investigating the filtration combustion in porous media described in [9-10], and to the model for investigating the gas flows through granular thermal storage phase-change materials described in [11-13]. So, the numerical method for proposed mathematical model is very similar to the one described in detail in [13]. According to the method, the energy equations, momentum conservation equation, equation for oxidizer concentration and equation of mass conservation for evaporated metal in gas are transformed into the explicit finite difference equations. When the solid temperature is not equal to \( T_{melt} \) or \( T_{evap} \), the summands with \( F \) and \( \partial \rho_{cm}' / \partial t \) in the energy equation for solid phase are equal to zero, and \( T_c \) is found from this equation. \( F \) or \( \partial \rho_{cm}' / \partial t \) are found from the energy equation for solid phase when the solid temperature is equal to \( T_{melt} \) or \( T_{evap} \) respectively. When the gas temperature is not equal to \( T_{evap} \), the summand \( \partial \rho_{gm}' / \partial t \) in the energy equation for gas is equal to zero, and \( T_g \) is found from this equation. \( \partial \rho_{gm}' / \partial t \) is found from the energy equation for gas when the gas temperature is equal to \( T_{evap} \). The continuity equation is transformed into the implicit finite difference equation. From this equation taking into account the perfect gas equation of state the gas pressure is determined using Thomas algorithm [14]. The remaining unknown quantities are determined trivially. The method is first-order accurate in time and second-order accurate in space.

3. Results of numerical calculations

Consider the porous object with impermeable non-heat Conducting side walls, which consists of the activated birch coal (combustible component) and firebrick crumbs (inert component) like in [15], and besides this the porous medium includes cadmium. Before starting moment, the pressure at the object bottom and top corresponds to the atmospheric pressure at assigned heights, so there is no air motion in the object. At the starting moment the pressure at the object bottom rapidly increases up to \( p_{01} \) and remains constant; the pressure at the object top \( p_h \) does not change. At the same time in the place of ignition, which has height \( H_1 \) and is located at the object bottom, the temperature of solid phase reaches a value \( T_{c0} \) and burning is started. Unless otherwise stated, we will use the following parameter values:

\[ H = 1 \text{ m}, \ \rho_{cf} = a_{cf} \cdot 2.5 \cdot 10^2 \text{ kg/m}^3, \ \rho_{ci} = a_{ci} \cdot 1.3 \cdot 10^3 \text{ kg/m}^3, \]

\[ \rho_{cm0} = a_{cm0} \cdot 8.65 \cdot 10^3 \text{ kg/m}^3, \ a_{g0} = 0.3, \ a_{cf0} = 0.1, \ a_{cm0} = 0.01, \]
\[ c_g = 10^3 \text{ J/(kg K)}, \quad c_{cf} = 1.2 \cdot 10^3 \text{ J/(kg K)}, \quad c_{cf} = 1.4 \cdot 10^3 \text{ J/(kg K)}, \quad c_{cm} = 2.64 \cdot 10^2 \text{ J/(kg K)}, \]

\[ \alpha = 10^4 \text{ J/(m}^3 \text{ K s)}, \quad \beta = 20 \text{ J/(m}^2 \text{ K s)}, \quad \lambda_c = 1.1 \text{ J/(m K s)}, \quad \lambda_g = 3.4 \cdot 10^{-2} \text{ J/(m K s)}, \]

\[ c_{s1} = 1.458 \cdot 10^{-6} \text{ kg/(m s}^{1/2}), \quad c_{s2} = 110.4 \text{ K}, \quad k_1 = 10^{-8} \text{ m}^2, \quad \chi = 0.5, \]

\[ g = 9.8 \text{ m/s}^2, \quad R = 8.31441 \text{ J/(mole K)}, \quad M = 2.993 \cdot 10^{-2} \text{ kg/mole}, \]

\[ Q_{comb} = 3.28 \cdot 10^7 \text{ J/kg}, \quad Q_{melt} = 5.393 \cdot 10^4 \text{ J/kg}, \quad Q_{evap} = 5.216 \cdot 10^5 \text{ J/kg} \]

\[ k = 1.6 \cdot 10^4 \text{ 1/s}, \quad E = 9.8 \cdot 10^4 \text{ J/mole}, \quad D_{g0} = 1.82 \cdot 10^{-5} \text{ m}^2/\text{s}, \quad b = 1.724, \quad \mu_g = 2.667, \]

\[ T_{g0} = 300 \text{ K}, \quad C_0 = 0.23, \quad T_{c0} = 900 \text{ K}, \quad T_{melt} = 594 \text{ K}, \quad T_{evap} = 1038 \text{ K}, \]

\[ p_{01} = 1.01 \cdot 10^5 \text{ Pa}, \quad p_h = 10^5 \text{ Pa}, \quad H_1 = 0.1. \]

Computational results obtained by means of the developed numerical model in 1D case are compared with the calculation results of heterogeneous combustion of the same porous media under the same conditions, but without metal (cadmium). Figure 1 depicts the solid phase temperature in the porous object for various volume concentration of condensed metal \( a_{cm0} \) at various times. As seen from the figure, the numerical solution of heterogeneous combustion of the porous object with metal is close to the combustion process without metal, but has differences.

Figure 2 shows the effective (or bulk) density of condensed metal (i.e., the product of phase density of cadmium and its volumetric concentration in solid phase). As seen from the figure, due to evaporation and condensation, condensed metal can be concentrated near the front of the combustion wave. This may allow to create zones with high metal concentration by means of changing the conditions of combustion. It should be noted that due to the chosen ignition conditions, a slight unburned zone remained in the left boundary of the object, in which the metal also remained; if the ignition conditions change, it is possible to achieve complete burnout of the object.

**Figure 1.** Solid phase temperature \( T_c \) versus distance from the bottom of the porous object \( x \) for various volume concentration of condensed metal \( a_{cm0} \) at various times \( t \).

**Figure 2.** Effective density of condensed metal \( \rho_{cm} \) versus distance from the bottom of the porous object \( x \) at various times \( t \).
4. Conclusions
A novel mathematical model is proposed for describing the time-dependent filtration combustion of metal-containing mixtures. For investigating the processes in 1D case, the numerical method has been developed and implemented, which is based on a combination of explicit and implicit finite difference schemes. The carried out numerical calculations have shown the efficiency of the proposed model and allowed to detect the concentration of the condensed metal near the front of the combustion wave.

Acknowledgements
The work was supported financially by the Russian Foundation for Basic Research (project 18-29-24029-mk). The results were obtained using the equipment of Shared Resource Center "Far Eastern Computing Resource" IACP FEB RAS.

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