

Mass Transfer in Filtration Combustion Processes

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1. Introduction

Wave combustion is one of wide-spread regimes of chemical reactions progress in the systems with the enthalpy excess. Combustion waves in porous medium have some special features, that let consider them as especial kind of combustion processes. Usually one denominates the filtration combustion (FC) as the oxidation of any solid combustible at gaseous oxidizer filtration. The presence of two phase states, intensive heat- and mass exchange between these two phase states, a constant countercurrent flow of solid and gas phases complicate considerably theoretical description of FC wave, as well as experimental results explication. In such systems one has to consider not only heat and concentration fields, but also the gas flow dynamics and heterogeneous reactions peculiarities. Besides it a huge difference between densities of components provides the necessity of common consideration of processes with appreciably different characteristic rates. Anyway due to some peculiarities filtration combustion waves remain very attractive objects for industrial application.

Combustion regimes with heat accumulation occupy an especial place in wave combustion processes. A typical example it is the combustion of a solid fuel at gas oxidizer filtration, when the combustion front direction coincides with the gas flow one (Aldushin et al., 1999; Hanamura et al., 1993; Salganskii et al., 2008). In coordinates, cohered with the combustion front (zone of the exothermic transformation) this process may be considered as the interaction of gas and condensed flows, coming from the opposite direction, passing through the chemical reactions zone, and being transformed in this zone with the change of both chemical content and physical-chemical properties (Fig.1).

The presence of high temperature area with an intensive interphase mass-transfer processes between counter-current phases flows forms a zone structure. In each zone there are physical and chemical processes depending on corresponding conditions (temperature, medium properties, reagents concentration etc.). Space separation of zones supplies an accumulation of either, one or another substance in the definite zone accordingly to his physical-chemical properties, and provides possibility of some useful components extraction. These peculiarities allow to realize some industrial processes in extremely effective and a low-price regime, basing on heat-effectiveness of combustion wave. Examples of FC processes industrial application are known. It is waste extermination using superadiabatic combustion (Manelis et al., 2000; Brooty & Matcowsky, 1991) underground oil recovery (Chu, 1965; Prato, 1969), metallurgical burden agglomeration (Voice & Wild,

1957; Zhu-lin, 2006) oxidative catalyst regeneration (Kiselev, 1988), self-propagating high temperature synthesis (Merzhanov & Borovinskaya, 1975; Novozhilov, 1992) etc. These processes are typical examples of FC with counter-current flow and superadiabatic overheat.

We have to notice that in this paper we consider heterogeneous combustion only. We do not consider the FC of gases where preliminary mixed gaseous fuel and oxidizer burns in porous heated medium (Babkin, 1993), because in these systems heterogeneous processes are not determinative.

Due to the wave structure the heat, released in chemical reactions, transfers intensively to source materials with no use of outside heat-exchange devices, only because of extremally intensive interphase heat-exchange while gas filtration. The heat accumulation may be so considerable that combustion temperature can exceed by several times the adiabatic temperature, when it calculated assuming that the initial temperature of any portion of reacting compounds is equal to the ambient temperature. That is why sometimes one uses the terms «superadiabatic heating», «superadiabatic regime of filtration combustion», or simply «superadiabatic combustion».

The term «superadiabatic» seems disputable at first glance, however any heat recuperation from combustion products to initial substances can increase the adiabatic temperature (Wainberg, 1971) of the mixture. Really due to an intensive interphase heat exchange in such system the temperature of initial interacting compounds is far higher than the ambient temperature and may approach the combustion front temperature. Anyway the term «superadiabatic» has been used during many years and we guess one should not replace it.

Just in superadiabatic regime the effectiveness of the heat recuperation may be maximally high, whereby namely when the solid combustible contains enough high amount of an inert material, and when the gaseous oxidizer contains enough high fraction of inert gas component (Salganskii et al., 2008). It is due to the FC process organization – inert components are very effective heat carriers, thus both combustible and oxidizer can be overheated maximally before they enter into the zone of chemical reactions. Solid combustible is heated due to gaseous combustion products, while gaseous oxidizer – due to ash residue and solid inert material.

The most interesting peculiarity of combustion waves in such systems is the independence of the stationary combustion wave temperature on the value of the reaction heat release (if it is a positive value). After ignition the temperature in the combustion front increases until the heat input (due to exothermic reactions) is equal to the side heat losses. Minimizing side heat losses the thermal equilibrium is reached at very high temperature, enough for considerable increase of chemical reaction rates. So, heat losses in FC processes play more important role than in case of classic combustion waves, because in the case of FC the heat losses determine to more considerable degree the temperature in the reaction zone. Temperature profile of such combustion wave is shown schematically in Fig.2. Due to an intensive heat exchange between source reagents and combustion products the released energy is accumulated mainly close to the combustion zone. If the mixture has a small heat release value (e.g. a mixture of carbon with a high amount of an inert material) the FC process will accumulate the heat energy with a lower rate and therefore it will reach the stationary regime longer.

At conditions of counter-current flows of combustible and oxidizer the combustion rate (that is very important characteristic) is determined mostly not with the heat transfer rate, but with the rate of reagents supply into the combustion zone (that is with the filtration rate).

Besides, before the combustion zone (in Fig. 1 and 2 - to the right of the high temperature area where the main chemical exothermic reactions run with highest effectiveness) the reducing zone exists with high amount of combustible and rather high temperature, that results in complete gaseous oxidizer consumption. Behind the combustion zone (in Fig. 1 and 2 - to the left of the high temperature area), contrariwise, there is a hot zone with high content of oxidizer, that provides the completeness of the material burning. In view of the aforesaid, it is obvious that the FC process is very attractive for industry, particularly when it is needed

- To burn cheaply a material containing small amount of combustible
- To obtain high combustion temperatures,
- To provide maximal fullness of solid fuel burning,
- To get space separation of zones (heating, pyrolysis, evaporation, oxidation, condensation, cooling etc.) in solid porous fuel.

Hereby the energy outlay may be minimal due to effective heat recuperation in FC waves.

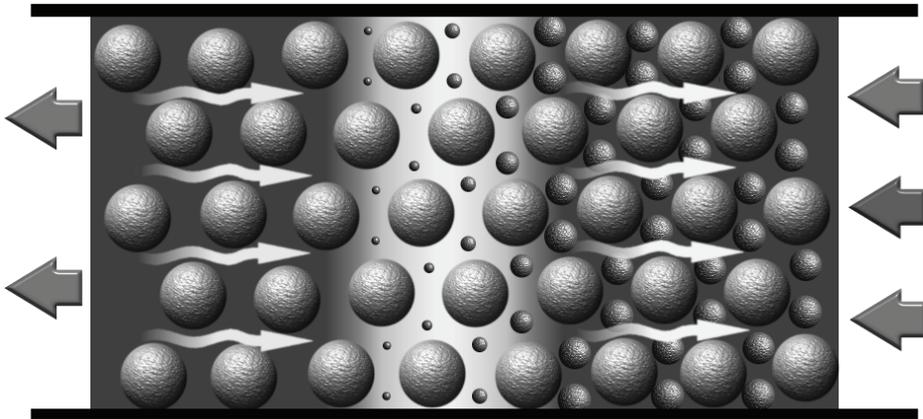


Fig. 1. Schema of combustion wave with superadiabatic heating. The solid combustible material - small balls, while the inert material - big balls. The solid material flow - right to left, the gas flow - left to right. High-temperature zone - the area with more light background

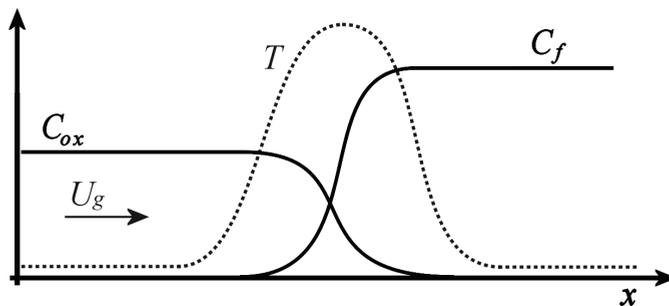


Fig. 2. Temperature and concentration profiles of the combustion wave in case of equal heat capacities of the flows of condensed and gaseous phases

2. Peculiarity of the physical and chemical structure of FC

2.1 The simplest case of FC process

There are many possibilities to realize mass transfer in FC processes. The simplest case in one-dimensional approximation is the chemical interaction of counter-current of solid fuel flow with gaseous oxidizer (being filtrating through the solid material) flow when a single combustion product forms. We are expecting the presence of both inert material in the solid fuel and other gaseous components (that do not participate in chemical reactions, e.g. nitrogen) in gaseous oxidizer. Hereby, depending on the phase state of the combustion product, this product is added to the respective flow through the reaction zone. For example, at carbon oxidation the combustion product is gaseous carbon dioxide, while at aluminum oxidation it is solid aluminum oxide. So, we have an interphase mass transfer of either solid fuel to gaseous product (Fig. 3b) or gaseous oxidizer to solid product (Fig. 3b). In both cases the whole redox process and the summary heat release are concentrated in the single reaction zone.

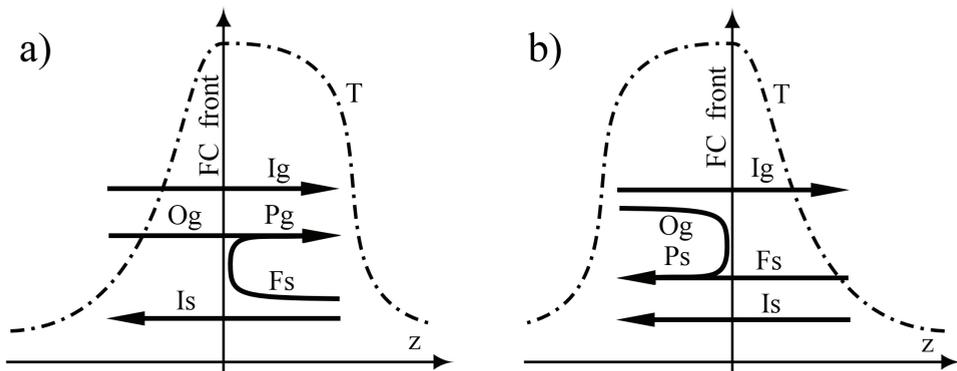


Fig. 3. Mass flows through the reaction front in cases of: a) gaseous products (P_g) and b) solid products (P_s). O_g and I_g - gaseous oxidizer and inert; F_s and I_s - solid fuel and inert substances, correspondingly

Let's presume that the temperature level in the reaction zone is enough high, it allows to consider this zone width being negligible small in comparison with the warming-up zone of the combustion wave. Besides we presume that the interphase heat-transfer at the filtration process is so effective that the difference between temperatures of solid and gaseous phase is negligible. Then depending on real conditions (combustible concentration in the solid mixture and oxygen concentration in gaseous oxidizer) the heat structure of the FC wave may be either like the curve in Fig.4a ("reaction trailing" structure), or like the curve in Fig.4b ("reaction leading" structure). The type of the heat structure is determined with the ratio of heat capacities of counter-current solid and gas flows through the reaction front (Aldushin et al.,1999; Salganskii et al., 2008). The heat, released in combustion, is removed with the gas flow in the case of the reaction trailing structure, while in the case of the reaction leading structure it is removed with the solid material flow. These two heat flows determine the type of the profile of the FC wave. It is possible that two these heat flows are equal, it provides a symmetric profile of the combustion wave and maximal heat accumulation in the combustion wave [Aldushin et al.,1999]. In this case the heat of

chemical reactions is removed with both solid material and gas. In all considered cases an intensive interphase heat-transfer results in the accumulation of all released heat near the combustion front. If the reactor is long enough, all products leave it at the initial temperature. Continuous heat energy accumulation results in the expansion of the warming-up zone in the direction either of the solid material or gas flow depending on the type of the heat structure of the FC wave. When side heat losses exist, a stationary profile of combustion wave can form. When side heat losses are negligible, a stationary process is possible at uncompleted heat-transfer only, in this case either gas or solid material leaves at hot temperature.

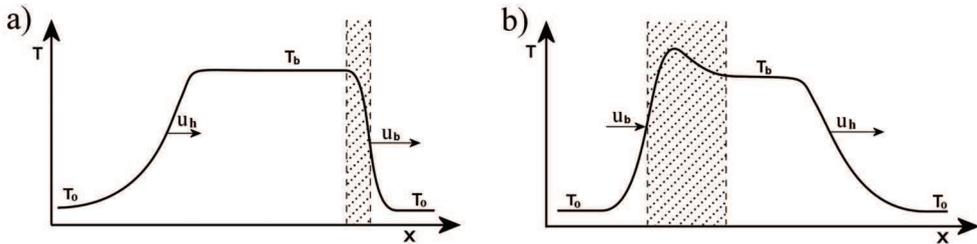


Fig. 4. Temperature profiles of combustion wave in case of there is no heat losses: a) – reaction leading heat structure, b) – reaction trailing structure. Hatches indicate zones of chemical reactions

2.2 Attended processes of evaporation and condensation

The heat structure of the FC wave determines conditions of compounds heating at combustion wave propagation, and all accompanying physical and chemical processes. For example, the presence of an additional volatile component in the solid fuel (besides the combustible itself and an inert material) results in the localization of the zone of this component concentration (evaporation – condensation) in the region of the fuel warming-up (Fig. 5a). The main heat release, providing the existence of whole FC wave structure, takes place in the combustion front. Evaporation process occurs due to convective heat flow from the combustion front. Mass transfer of the vaporized component with the gas flow takes place before the area of condensation. If the convective heat flow from the combustion front is higher than heat losses for the evaporation, the zone of the accumulation of the vaporized component expands. If there are side heat losses the expansion of this zone ends sooner or later, and further all processes set moves stationary as a batch.

In the case of the reaction leading structure, the evaporation zone is situated near the combustion front, which determine and provide the FC wave structure. Therefore considerable heat expenses for the evaporation may decrease the combustion front temperature, and surely it has an influence on all characteristics of FC waves. In the case of reaction trailing structure, the heat expenses for the component evaporation decrease the temperature in the region of warming-up, not in the combustion front, therefore these heat expenses do not influence the value of heat release in the combustion front. It is an extraordinary peculiarity of these regimes of the FC. The zone of condensation of vaporized component is situated a bit farther along the gas flow. The condensation process is accompanied with some heat release, therefore in this case there is not mass transfer only, but heat transfer from one zone to another one too.

Typical example of vaporized component presence is the fuel moisture. Due to superadiabatic heating it is possible to organize the FC regimes where high content of moisture does not prevent propagation of stable combustion wave (Salganskaya, 2008).

It is not necessary that the condensation of the vaporized component occurs always to its accumulation in the determined reactor zone. For example, the water condensation occurs to an aerosol forming. The higher size of drops of the liquid, the easier they sediment on the initial solid material during the filtration process. Temperature gradients in the FC wave may be very high. In this case a high rate of the gas cooling occurs to forming very small drops (less than 10^{-6} m), which sediment badly under filtration and may be removed (as a fog) from the reactor with the gas flow. Thus, it is rather simple to organize the extraction of a volatile component from the source solid material.

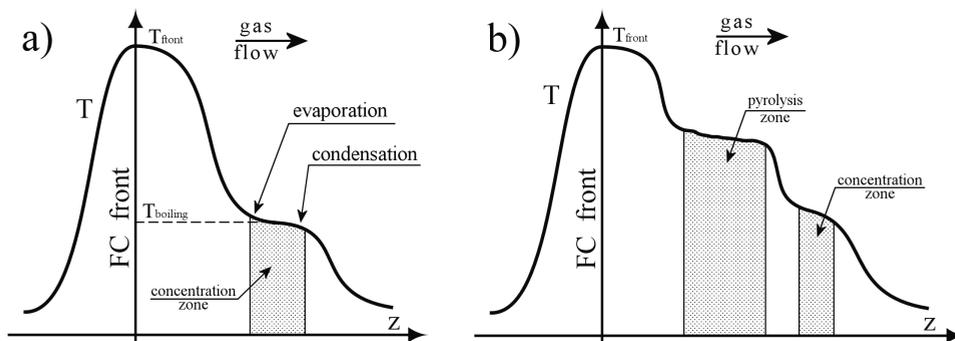


Fig. 5. Heat structure of the FC wave, propagating through a porous solid fuel: (a) – in case of an evaporating component, and (b) – in case of pyrolytic decomposition of the fuel

2.3 Peculiarities of filtration combustion of carbonic systems

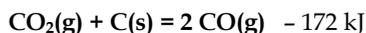
Layer burning of carbonic fuel has been used long since, and many systems of gas generators, industrial furnaces work still using this process. The combustion of porous burden containing solid carbonic fuel and incombustible material at air or another oxygen-containing gaseous oxidizer filtration is of great interest for industrial application in processes of solid fuel burning optimization, as well as for developing environmentally friendly methods for different combustible wastes recycling.

Heterogeneous carbon oxidation is a complicated and multistage process. The final product are carbon dioxide and monoxide. There is no sure answer which one of these two oxides is the primary product of the carbon particles oxidation, and which one forms already in the gas phase. It is so difficult to find out it because as soon monoxide forms it may be oxidized immediately to dioxide, while dioxide at rather high temperature may be reduced to monoxide above carbon surface. Currently most part of researchers guess that in result of heterogeneous processes two oxides form together (Lizzio et al., 1990; Bews et al., 2001; Chao'en & Brown, 2001). Oxidation mechanism and the quantitative ratio of formed oxides depend on conditions (temperature, pressure etc.) as well as on properties of carbon particles surface.

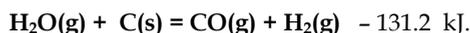
At the interaction of the main components of FC in counter-current flows of solid fuel and gaseous oxidizer, a zone structure forms, each zone differs from another one in temperature and reagents concentrations. In the main zone of heat release (combustion front) carbon is

oxidized to CO and CO₂. In case of "reaction leading" wave structure solid combustion products near combustion front stay in oxygen medium at high temperature, that's why here carbon burns completely. However it is possible that oxygen is not expended completely because a quickly gas flow cooling behind the combustion front may occur to oxidation reactions deceleration.

In case of "reaction trailing" wave structure the appearance of mass transfer is entirely different. Solid products, leaving the combustion front, cool abruptly. Hereby regimes with incomplete carbon combustion are possible. Contrariwise, gaseous combustion products get through high-temperature area with big amount of hot carbon. It leads to complete oxygen exhaust, as well as to forming the zone of endothermic reactions, where carbon dioxide may be reduced to monoxide:



Besides if water steam there is in gaseous oxidizer (steam-air gasification), other very important reaction proceeds in the same zone on the carbon surface:



These reactions proceed with considerable rate only at enough high temperature, therefore they decrease local temperature in the hottest places. Hereby two combustible gases appear in gaseous combustion products: an additional carbon monoxide, and considerable amount of hydrogen (at steam-air gasification up to 30 vol.%). So, depending on conditions the FC of carbonic systems can proceed by considerably different ways, and with different results. These peculiarities of the heat structure of the FC waves at carbonic systems combustion have to be considered at industrial realization of technologies based on superadiabatic condition regimes.

2.4 Attended processes of thermal decomposition at filtration combustion wave

The structure of the FC waves may be rather complicated. The main heat release in the combustion front determines the common temperature level. When components predisposed to thermal decomposition there are in the solid fuel, a new zone forms in the combustion wave structure: zone of corresponding chemical processes. For example, if there is calcium carbonate (chalk, buhr) in carbonic fuel, during the heating it will decompose in a varying degree, dependently on temperature. Hereby solid combustion product (quicklime) remains in the burden, while gaseous carbon dioxide removes together with other gaseous combustion products. Fig.6a shows the results of the thermodynamic calculations of the equilibrium $\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$ at the pressure 1 atm in air medium at temperatures since 800 up to 1200 K. On the other hand if for example there is copper oxide CuO in the burden, CuO begins to decompose (Fig.6b) at high temperature (higher than 1400 K) and an additional oxygen appears in gaseous combustion products, then this oxygen reacts immediately with the fuel. In this case the combustion wave structure is complicated because of two new zones (the zone of CuO decomposition and an additional zone of the fuel oxidation) appearance. Hereby in each zone individual physical and chemical processes proceed accordingly the temperature level and reagents concentration.

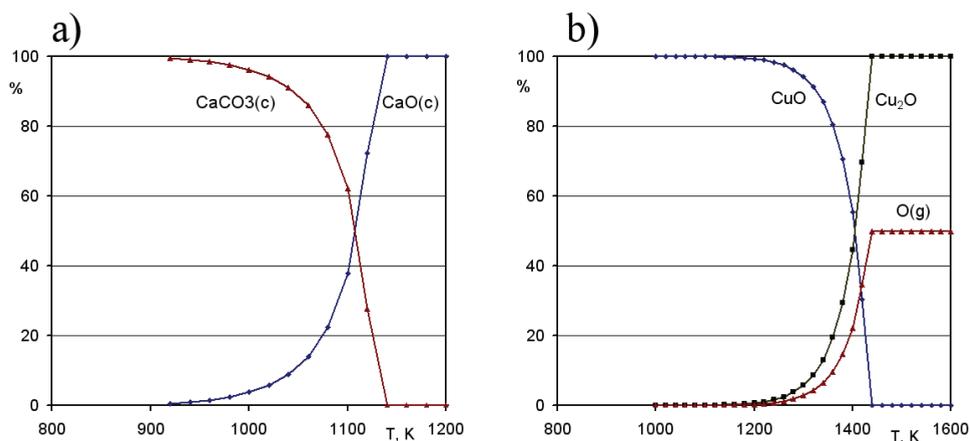


Fig. 6. Thermodynamic equilibrium in systems containing CaCO_3 (a) and CuO (b)

In this system mass transfer may be too complicated. Details of the temperature profile of the complex combustion wave reflect all processes with heat release and heat absorption.

2.5 Filtration combustion of fuel able to pyrolytic decomposition

Filtration combustion of organic fuel is a particular case of combustion wave with thermal decomposition processes. Being heated these fuels usually pyrolyze forming liquid and gaseous products, as well as coke residue. Typical examples are organic fuels: wood, peat, natural coals etc.

In this case the heat wave structure is complicated – a new zone of thermal decomposition appears before the combustion front (Fig. 5.b). Pyrolysis proceeds in the zone of solid fuel warming-up where no oxygen presents. Usually thermal effect of pyrolysis is rather small in comparison with heat release in the combustion front.

Usually solid coke residue, pyrolysis tars, and gaseous destruction products form during the pyrolysis. Then the coke falls into the combustion zone and burns there. At relatively high temperature pyrolysis tars stay in gas state and move with the gas flow and gaseous pyrolysis products from pyrolysis zone into the region with lower temperature. There the pyrolysis tars, which is a mixture of different hydrocarbons, condense. It provides appearance of zone of liquid products accumulation, like the zone of the volatile components accumulation, but with the only difference – the origin of the products accumulated in these zones is different.

The content of pyrolysis tars is rather complicated and it may be different depending on the nature and properties of the material under pyrolysis, as well as on the rate and intensiveness of the heating. There are thousands of organic substances in pyrolysis tars, among them many toxic substances. The worth of these tars is not considerable because in order to obtain any goods (e.g. motor-fuel) it is necessary to organize rather complex chemical processes. So, at this stage it is appropriate to burn pyrolysis tars and to obtain heat or electric energy. However we have to consider the possibility to develop technology of liquid fuel producing from non-petrolic source, moreover this source may free, even have a negative price (if one utilizes some kinds of organic waste).

Pyrolysis tars, which condense in gas flow at its cooling, form aerosol by the same way as volatile components do. And by the same way pyrolysis tars may be removed (as small fog drops) together with the gas flow from the reactor (Salganskii et al., 2010). Unlike moisture and other incombustible components, pyrolysis tars are combustible and may be burnt in presence of gaseous oxidizer.

3. Characteristics of filtration combustion of some metal-containing systems

Investigations on FC processes showed (Manelis et al., 2006) that this process may be successfully used for some metal extraction, namely metals, which can form relatively volatile products (products of oxidation as well as of reduction), because even at their low concentration in the gas phase they may be removed together with gas flow, shifting the thermodynamic equilibrium to the needed direction. The most interesting is the realization of FC in superadiabatic regime for extraction less-common metals from unconventional sources – poor ores, burrows etc.

Mass transfer of different metal derivatives in the FC waves may be successfully realized because the pressure of saturated steams of some metals themselves and some of their derivatives at temperatures from 800 to 1200°C (typical temperature for FC processes) is enough for their extraction. As objects of this kind of mass transfer may be considered some free metals (**Zn, Cd, Hg, As, Se, Tl, Ta**) as well as some oxidized forms (trioxides of molybdenum and rhenium, oxides of selenium, tellur, tantalum, tungsten hydroxides). New possibly appears to develop effective technologies for extraction valuable metals from unconventional sources.

All physico-chemical processes said above, which can realize mass transfer and extraction of valuable metals, may be realized without using filtration combustion, that is by known methods, but only in superadiabatic regime of FC due to maximal level of heat recuperation, and therefore due to maximal heat efficiency, it is possible to realize the same processes with minimal energetic expenses, that is maximally effectively from an economic point of view.

Naturally, mass transfer of relatively volatile substances from the reaction zone is accompanied with incessant processes of evaporation (as the zone of this substance staying is heated) and condensation (as steams of this substance falls into the zone with lower temperature). So, when a few products move from the initial mixture they may be separated spatially depending on their volatility, adsorption coefficients etc. Fig.7 demonstrates that in FC of mixture where, besides fuel and inert material, additionally iron, zinc, and cadmium (iron is not volatile, cadmium volatility is far higher than zinc volatility) present, the iron concentration does not change, while concentration of zinc and cadmium change so manner, that there is an incessant accumulation of these metals in determined places. The zone of cadmium maximal accumulation is farther from the combustion front than the zone of zinc maximal accumulation.

The fact that in filtration combustion process the whole reaction zone anytime is separated on two parts – oxidation zone and reducing one, is very useful if one considers filtration combustion regime as a way for metals mass transfer. All reactor volume is not uniform, there are zones with different temperatures and different redox nature of gaseous phase there. The zone left to combustion front (Fig. 3a) is the oxidizing zone, right to combustion front (Fig. 3b) – reducing zone.

This peculiarity should be used for the optimization of processes of different metals extraction. For example, when we extract molybdenum (**MoO₃** is far more volatile is

individual metal) we have to organize a combustion process in "reaction leading" mode (Fig. 4a). In this case Mo-containing products form in the oxidizer zone (naturally at rather high temperature though lower than combustion front temperature) relatively volatile MoO_3 which moves together with the gas flow behind combustion front.

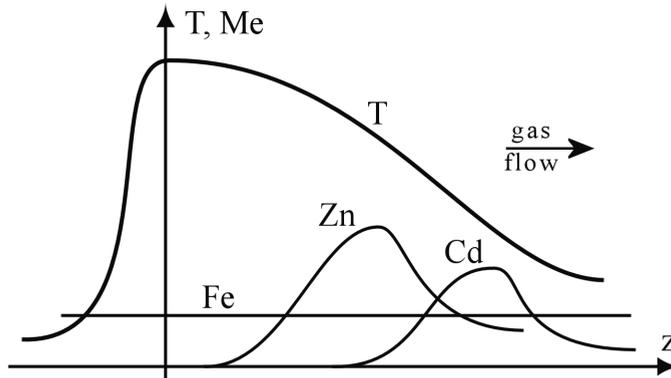


Fig. 7. Zones of metals accumulation separation in the wave of filtration combustion

When we want to realize mass transfer of metals having rather volatile reducing forms (e.g. free metals such as **Zn**, **Cd**) we have to organize FC in regime with "reaction trailing" structure. Then this compounds reduce with carbon monoxide before the combustion front in hot reducing zone (Fig.4b) and metal vapour moves together with gas flow and may be extracted or at least accumulated in burden portions left of combustion front.

A correct choice of combustion regime for realization of mass transfer of the giving metal may be obtained preliminary from results of thermodynamic calculations of equilibrium concentrations (e.g. using the code TERRA (Trusov, 2002)). For example, we are representing results of thermodynamic estimation of the system containing metallurgy tailing containing high amount of iron and zinc. We looked for the possibility to extract useful metals from secondary heavytonnage source (there are million tons of this kind of tailing in Russia only), which can not be recycled with economic effect using traditional technologies. One of real samples has been investigated, it contains (mass.%%): **Fe**-28.4; **Zn**-12.05; **Ca**-5; **Si**-2.65; **Mn** - 1.26; **Pb**-1.07; **Mg**-0.86; **Al**-0.2; **Cr**-0.16; **Cu**-0.11 and **P**-0.037. Thermodynamic analysis considered atmosphere pressure and temperature from about 500 till 1300°C with different oxygen concentration. As result we got the listing of possible reaction products and their equilibrium concentration in the given conditions. It gave the first resumes and ideas. It was shown that zinc and lead are the most interesting for their extraction using FC processes. **Zn** and **Pb** forms the most volatile substances. In oxidizing zone (Fig.8) practically all zinc stays in condensed phase (as $\text{ZnO}(c)$), so it is too hard to extract zinc using the regime "reaction trailing" structure of combustion wave. Changing the gas content in direction to **CO** excess, **Zn**-containing substances begin to be reduced starting from determined temperature and form free metal that moves to the gas phase (vapor pressure of **Zn** is 0.00002 MPa at 1200 K and 0.0001 MPa at 1300 K). If initial coal portion in the mixture increases (that is the ratio **O/Zn** decreases) **Zn** vaporizes at lower temperature (compare Fig 8b and 8c), and therefore it makes process of **Zn** extraction easier.

As for lead, unlike **Zn** even in oxidation zone there are enough **Pb**-containing substances (different oxides) in the gas phase, at temperature higher than ~1000°C practically a half of **Pb** is already in the gas phase, up to ~1400°C mainly in the forms of **Pb₂O(g)** and **PbO(g)**. Change of gas medium properties (in reducing medium) gaseous **Pb** appears beginning from ~800°C, and by ~1200°C it remains practically the only **Pb**-containing gaseous product (vapor pressure of **Pb** is 0.00016 MPa at 1200 K, and 0.0028 MPa at 1300 K). Unlike the case with **Zn**, systems, containing **Pb**, do not change with the change of reducing potential (compare curves on Fig. 8b and 8c, they are practically the same).

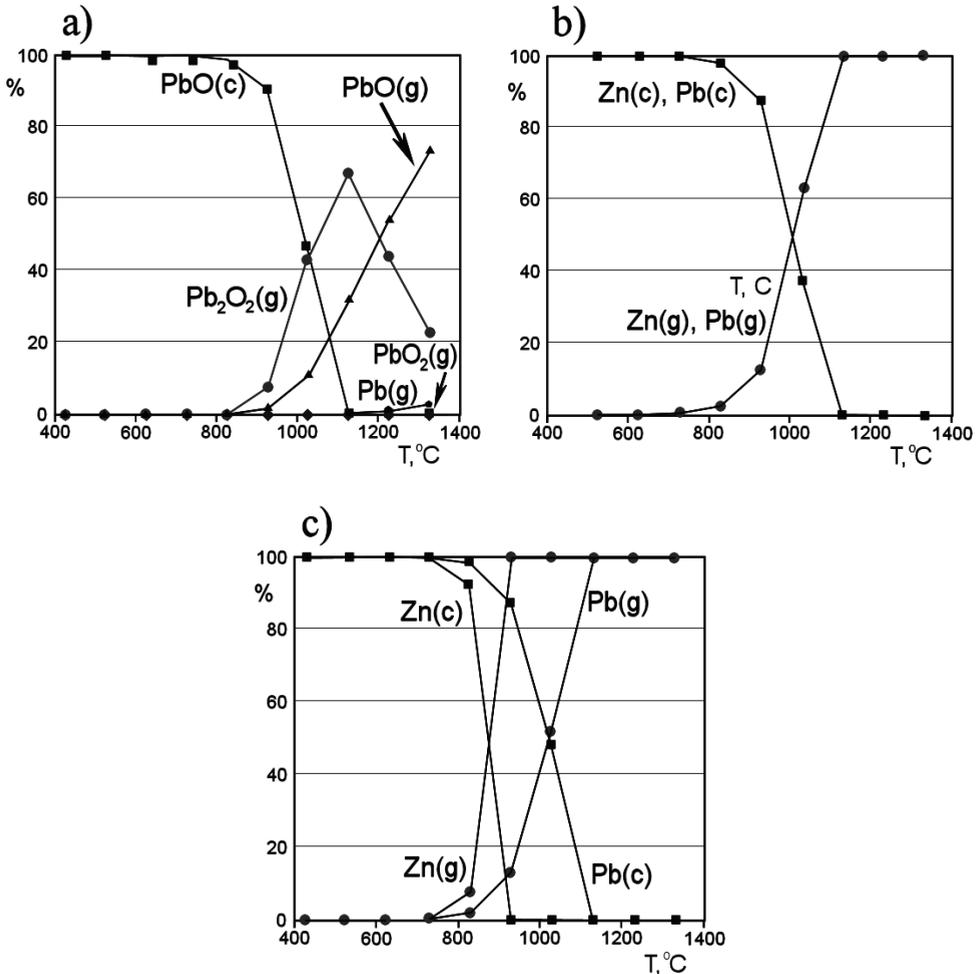


Fig. 8. Main substances, containing **Zn** and **Pb**
 a) in oxidizing gas medium with oxygen excess,
 b) in reducing gas medium, where the most part of carbon is in **CO**,
 c) in reducing gas medium, where the most part of carbon is in carbon itself

Thermodynamic analysis shows that other metals, represented in the tailing under consideration, practically do not form gaseous products neither in oxidizer zone nor in reducing one. So, it was theoretically shown that using FC it is possible to extract **Zn** and **Pb** from that tailing. **Zn** may be extracted when relatively high temperature there is in the reducing zone (that is at "reaction trailing" wave structure) while **Pb** may be extracted using both regimes - "reaction leading" or "reaction trailing" wave structures. In case of "reaction leading" wave structure lead oxides will leave, while in case of "reaction trailing" - gaseous lead.

Above in section 3 we discussed only systems containing a few metal in mixture with organic fuel, inert material and air, that is systems **C-N-H-O-Me**. But there are few metals and metal oxides, having rather high vapor pressure at temperatures lower 1200-1300° C (at higher temperatures it is hard to organize industrial processes that would be economically acceptable). The listing of such metals includes mainly **Zn, Cd, Hg, Te, Tl, Se, As, W, Re, Pb**. However this listing may be considerably expanded if we introduce chlorine or fluorine into the system, that is if we consider the possibility of mass transfer of gaseous chlorides and fluorides (chlorides and fluorides of few tens metals are rather volatile at temperature lower than 1200°C). So, potential abilities of FC processes would be strongly enlarged, but we will meet another serious drawback - presence of chlorine, moreover fluorine, creates problems in environmental protection. We only recently began to investigate FC processes of systems with chlorine (Balabaeva, 2009) and we do not consider these systems in this paper. We have to notice a special case of fuel, metal sulphides, e.g. molybdenum sulphide (**MoS₂**), arsenic sulphide (**As₂S₃**). It was shown (see infra section 3.1) that at FC of mineral molybdenite concentrate (**MoS₂**) it is possible to organize an effective FC process with no additional fuel, hereby relatively high volatile molybdenum trioxide removes from the initial burden. Some examples of the effectiveness of the FC process are described below (sections 3.1-3.3).

3.1 Trioxide molybdenum extraction from mineral molybdenite

Experimental testing of **MoO₃** mass transfer possibility at FC of molybdenite has been realized using flotation concentrate of mineral molybdenite (by ~50% **Mo**). FC process needs a good gas penetrability of the solid reaction mixture, therefore the initial material has to be granulated in order to provide a rather quickly and stable air flow through the burden. Flotation concentrate of mineral molybdenite has been granulated with bentonite clay, obtained granules (2-4 mm diameter) contained by 40-50% **Mo**. FC process was realized in a model vertical quartz reactor length ~500 mm, diameter ~20 mm. The reactor had a system of preliminary ignition from an outside thermal source, which was installed before (lower) the main burden mass. Reaction temperature was measured using a set of thermocouples, installed in a few places in the burden in different distances from the combustion start. After the mixture is burnt and the residue is cooled a few samples from different places in different distance from the combustion start have been analyzed. Sublimated products were analyzed too.

Depending on combustion conditions (air flow rate, burden content etc.) the combustion front velocity was between 3 and 7 mm/min. For burden with no additional coal (if molybdenite content in the mixture is rather high, the heat of its combustion is enough to support a stable filtration combustion front without additional fuel) and no inert component the increase of air flow rate from 0.6 to 1.1 m/s increases combustion front velocity from 3.8 to 6.6 mm/min, hereby the maximal temperature in the combustion front increase too (from

900 to 1300°C). Addition of coal (up to 20%) into the initial mixture changes the character of the temperature rise – after its strong increase there is a period of slow rise up to the maximal value.

Addition of the inert material changes the combustion temperature at the same gas flow rate. In this case temperature profile has a practically symmetric form, which characterize the optimal superadiabatic regime, maximal temperature was about 1100°C.

Chemical analysis showed that by burning molybdenite in FC regime it is possible to obtain molybdenum trioxide of high purity. Hereby we did not notice undesirable caking of the burden. Almost half (56-57%) of obtained molybdenum trioxide did not leave the reactor and remained in the calcine. After processing all this molybdenum trioxide can be moved in a solution form by the water ammonia, and simply extracted.

3.2 Filtration combustion of mixtures containing used catalysts with molybdenum

Aluminosilicate catalysts doped with nickel, and containing 11-12% MoO_3 (spent catalysts are tonnage wastes after industrial petrochemical synthesis processes) have been investigated as a secondary source for molybdenum recycling. In order to burn this material it is already necessary to add a fuel into the burden because the catalyst itself does not contain any combustible compounds. In case of this material burning in the FC regime, one does not need to add another solid inert compound, because the catalyst itself serves as inert material (it contains up to 80% inert aluminosilicate). Granules with catalyst and bentonite clay (similar those describing in section 3.1), mixed with coal (at different ratio) were burnt in the same maner as granules with molybdenite were executed. It was found that at coal content 3-10% in the solid mixture the filtration combustion process goes in stable regime [3]. At constant air flow (about 0.7 m/s) the increase of coal content in the initial mixture from 3 to 10% results in practically linear increase of maximal temperature in combustion front (from 600 up to 1340°C). Gas flow rate increase do not influence practically the maximal temperature. Increase of the coal content as well as the air flow rate rises the combustion front velocity practically linear.

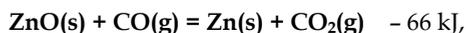
During combustion process a white deposit forms at «cool» reactor walls, far from hot zone this deposit becomes gray. Chemical analysis showed that it is mainly molybdenum trioxide. Totally 78% of molybdenum went to sublimate. Optical microscope tests in transmitted and polarized light showed that products of the combustion of **Mo**-containing systems, taken from reactor walls, are transparent crystal powders containing needle-like particles of lenth 50 μm to 1-2 mm and width 10-20 μm . Analysis shows that samples of the sublimate crystals taken out of burden zone contains higher than 95% MoO_3 .

It was shown that at the end of combustion process the content of MoO_3 increases on approaching to the final end of the burden, but it is always lower than molybdenum concentration in the initial mixture, that proves once more that mass transfer of **Mo**-containing derivatives left the initial reaction mixture. An interesting regularity was observed: maximal yield of **Mo** into sublimate occurs at coal content 5-6% (combustion front temperature is 850-950 °C), the increase of coal fraction up to 8-10%, and correspondingly, combustion front temperature up to 1000-1340°C makes the yield considerably lower. It seems that at coal content increase the heat structure of the combustion wave changes from "reaction leading" (at low coal content) to "reaction trailing" (at coal content increase). In the last case the reducing zone becomes more heated and molybdenum oxides may be reduced there to metal molybdenum which is not volatile in these temperatures. Another possible reason of MoO_3 yield fall at $T = 1000\text{-}1340^\circ\text{C}$ may be any change of crystal structure

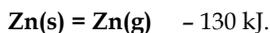
of aluminosilicate cage of catalyst structure at intensive heating and as result an aggravation of conditions for MoO_3 mass transfer.

3.3 Filtration combustion of mixtures containing zinc

Experimental investigations of FC and mass transfer of Zn-containing products have been carried out with a wide set of model mixtures, including zinc as a free metal as well as zinc oxide (ZnO). It was shown that by the control of the filtration combustion process organization (varying control parameters in wide interval, that is changing the coal content from 10 to 40%, and air flow rate from 0.01 to 1.8 m/s) it is possible to optimize FC regime with reaction leading structure (ZnO extraction) as well as regime with reaction trailing structure, where the reducing of ZnO to free Zn is possible due to endothermic reactions



with further zinc sublimation:



Stable combustion regimes for the systems under investigation were found at air flow rate higher than 0.06 – 0.11 m/s. Hereby temperatures of combustion front at the tested interval of controlling parameters reached 690 – 1300 C and increased with the fuel content rise as well as with air flow rate increase. For all samples under consideration combustion front velocities were between 0.7 and 17.5 mm/min and they increased with the air flow rate rise at the constant fuel content.

It was shown that the depth of ZnO extraction to the sublimate depends on initial zinc content in granules of Zn-containing burden component. During the burning of systems, containing many ZnO (10-30%), we found that the concentration of ZnO in the burnt mass decreased from the start point of combustion to the end point if the air flow rate was rather small (lower than 0.1 m/s); at higher air flow rates (0.4 – 1.7 m/s), conversely, ZnO concentration increased from the start point of combustion to the end point. It proves that Zn-containing combustion products move through the burden. Increase of combustion front temperature rises the level of Zn extraction from the system and this yield was between 3 and 34% depending on many factors.

For systems with small zinc content in the burden (2-4%) the level of zinc extraction depends on air flow rate and on fuel content, at small flow rates the effectiveness of Zn extraction reached sometimes 100% or so.

4. Principal advantage of filtration combustion over traditional methods of substances extraction

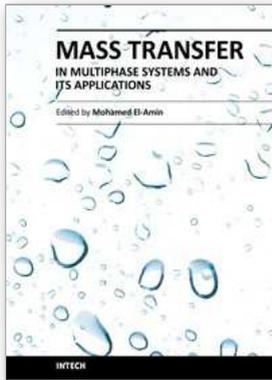
We have to stress once more: all processes of the mass transfer described above may be executed in simple stove regime, that is heating all reaction mass in the media of necessary gas (depending on the type of the substance to be extracted, this gas may be air, carbon monoxide, hydrogen etc), but in this case we have to waste energy in several times higher than it is needed to proceed the same chemical reaction in superadiabatic regime using the method of filtration combustion. Incessant heat recuperation in filtration combustion wave and the fact that only a small part of all reaction mass is heated at the moment and the most part of the thermic energy moves along the reaction mass and do not disperse outside

provide high energetic efficiency of the process. By this way it is possible to realize mass transfer of different kinds of compounds able to form volatile products. Spending of energy for the mass transfer of compound to be extracted by the FC method are considerably lower than necessary spending for heating all reactive mass to obtain the same extraction effect. Moreover, filtration combustion process may become not energy-consuming, but even energy-generating if further one uses combustible gaseous products (CO , H_2) as fuel for other industrial goals (heating, eclectic energy obtaining etc.).

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