

INNOVATIVE THERMODYNAMICAL CYCLES BASED ON ENHANCEMENT MASS, MOMENTUM, ENTROPY AND ELECTRICITY TRANSPORT DUE TO SLIP, MOBILITY, TRANSPARATION, ENTROPY AND ELECTRIC JUMPS AS WELL AS OTHER NANO-FLOWS PHENOMENA.

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ABSTRACT

In our work, a further development of the authors model of thermo-chemical flow of fuel, air, oxygen, steam water, species, ionic and electron currents within nano channels and nano-structures of novel devices is presented. Different transport enhancement models are taken into account -among them the most important are: the velocity slip connected with complex external friction, the Darcy mobility and the Reynolds transpiration. Increasing gas path to the triple-phase-boundary (TPB) enhances mass and electricity fluxes due to the concentration jump and the electron resistivity jump. Enhancement of heat transport due to the von Smoluchowski jump is considered within the frame of generalized model of Navier-Stokes slip boundary condition. Particular elements of the model have been tested and calibrated on the literature benchmark experiments concerning nano-flows, nano-combustion, nano-condensation and separation. Integrated geometrical characteristics of working fluids and canal materials such as: porosity, tortuosity and mean radii are finally involved into a macroscopic continuum model, and implemented into the standard CFD code. As a result of analysis the production characteristics have been examined and compared with the benchmark data.

MOTIVATION OF OUR STUDY

Standing within the current clean coal technologies, the coal-fired power plants using carbon capture equipment becomes an expensive source of electricity in Poland. Other power sources, such as wind, nuclear, geothermal are in a starting level and cannot be taken to be a serious candidate to repowering of polish energy market. One of contra-candidate to the clean coal power plants are, at the moment, the plants based on natural and shale gases ei. the combined cycle with CO₂ capture technology that currently appear to be more economical [17].

Due to recent possibility, growing after discovery of Polish natural and unconventional gas sources, a new possibility of realistic huge cleaner than coal heat energy source will be obtainable in a few years. In this new chance for modern repowering of Polish energy system, as we assume, the steam turbines technologies should be widely used, firstly, for combined heat and power plants [16; 17]. The new candidates to repowering are plants based on the gas-steam combined cycles erragemed within innovative thermodynamical cycle based, generally, on using of different nanoflow phenomena. But in innovative combined cycle the role a steam turbine change radically. Now, unlike a gas turbine, in a steam turbine heat is only a byproduct of power, therefore in cogeneration, steam turbines generate reduced amount of electricity as a byproduct of heat contained in flue gases. Recall, that usually about 10 kg/s of flux of flue gases is needed for generating of 1 kg/s of fresh steam [4; 5; 15; 16]. In conventional combined cycle, a steam turbine is captive only to a separate heat source and does not directly convert fuel to electric energy. The energy is transferred from flue gasses to the turbine through a multi-pressure steam generator

(HRSG) [14; 15], and steam such produce, in turn, powers the turbine and generator. This separation of functions enables steam turbines to operate independently from the gas turbine. Therefore some advantages of steam turbines as for instance, unusually high drop of pressure from 22 MPa to 500 Pa cannot be fully explored in the whole conversion process¹.

In the following paper, one of innovative cycle is a compact combined cycles which turns combined heat and power plants to a power plant dedicated only to clean electricity production. It can be done by removing of the HRSG from a role of heat exchanger between the flue gases and working water, and to replace the combustion chamber on a internal direct steam producer [17]. Such combined gas and steam turbines can keep their main performance specifications like the high pressure (22 MPa) and high temperature (1100°C) - it is quite a new situation - up to now there is no steam turbine with such high temperature of working medium, and, vice versa, there is no gas turbines with such extremely high pressure. Since this concept can be simply and naturally connected with concept of oxy combustion there is a thermodynamical base for a zero-emission gas-steam turboset.

Especially, in next chapter, the particular analysis of gas-

¹Now, The basic question is - does clean gas technologies shall be economically substantial? The leading factor is the gas price due to Gasprom monopole. The hope on cheaper gas comes from the recent searches of the shale gas in the Pomerania district. The ability to economically produce natural gas from unconventional shale gas reservoirs in Poland, has been made possible recently through the application of horizontal drilling technology and so-called "hydraulic fracturing" (e.i. fracking, fracturing). Concerns like: Chevron, Exxon Mobil, ConocoPhillips, Marathon Oil, have already prepared this drilling technique which has revolutionized gas production in the United States. [17]

steam turbine within a zero-emission cycle will be presented. In that case, the working fluid contains only the mixture of CO_2 and H_2O what leads to direct separation of CO_2 [11; 12; 13].

Innovative cycles, concerned here, leading to high-efficient, zero-emission energy production and there are combined from simple cycles ordered in a conversion cascades [10; 8]. Typical for these cycles the enhancement of efficiency and power are to be obtained via compactification of devices dimensions and using of the so-called direct conversion. For instance, fuel cells are profitable modern devices being the best examples of a useful machinery where complex conversion of energy at nano-scale takes place. Especially, we observe such conversion at the high temperature solid oxide fuel cell (SOFC) that is built from ceramic nanomaterials. Anode supported fuel cell consist mainly of two nanoporous electrodes (cermets, lanthanum strontium manganite) separated by a thin, very dense solid electrolyte (yttria-stabilized zirconia or perovskite-type material). Finding of a mathematical model of an acting SOFC at temperatures as high as 1000°C is a serious challenge as well for nanomechanics as for nano-thermo-chemistry [10; 8].

ZERO-EMISSION CYCLE VIA A STEAM-GAS TURBINE

Concept of cycle based on enhancement energy transport

In principle the oxycombustion and capture of CO_2 can be accomplished more easily and cheaply than post-combustion removal of CO_2 from the exhaust gases emitted by a conventional coal plant. The promise of more efficient carbon capture is one of the primary rationales for clean gas technology (CGT). Ziólkowski et al. [17] has recently been prepared a concept of repowering of GT8C cycle. Their concept is based on introducing of compact nanotechnology devices leading to removing large-scale devices like Heat Recovery Steam Generator (HRSG) and Low Pressure Condenser (Fig. 1). The first is to exchange the combustion diffusional mode from the classical one into a one based on oxygen nano-enriched air. In this same place (MKS), phenomena of nano-removing of heat revised form oxygen-hydrocarbon combustion process occur which is governed by adequate steam injection (water-nano-jets) into the combustion zone. It leads directly to high enthalpy flue gases that contain only CO_2 and steam. The second novel element is a Dual Brayton Cycle used for steam condensation and compression of CO_2 . The enhanced condensation is based on nano-injection of cold water condensate and a jet compression of CO_2 (in SNS). Due to compactness of process within turbine low part and exhaust hood, as well as the heat recuperation high efficiency is obtained.

CFM simulation

By introducing enhancement transport and conversion integral-like coefficients into zero-dimensional model of thermodynamical cycle, it is possible to simulate the work of an innovative zero-emission power plant. A starting point for conversion of GT8C into zeroemission-GT8C has been taken as normal operating condition for PGE Gorzów. Data for numerical analysis of traditional GT8C have taken from literature [16]. Two different modernization of GT8C have been considered. Both modernizations are based on oxy combustion,

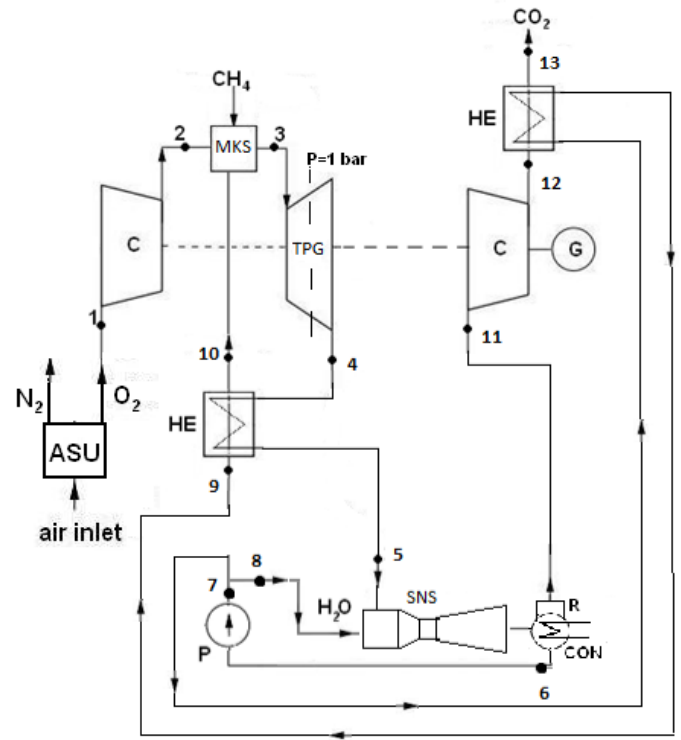


Figure 1. IFFM cycle to the compact, high efficiency and zero-emissions power plant, where the MKS - Wet Combustion chamber, TPG - Paro-Gas Turbine and SNS - Condenser spray-ejector, C - compressor, HE - heat exchanger, G - generator, P - pump and R - a gas-water separator, CON - condenser

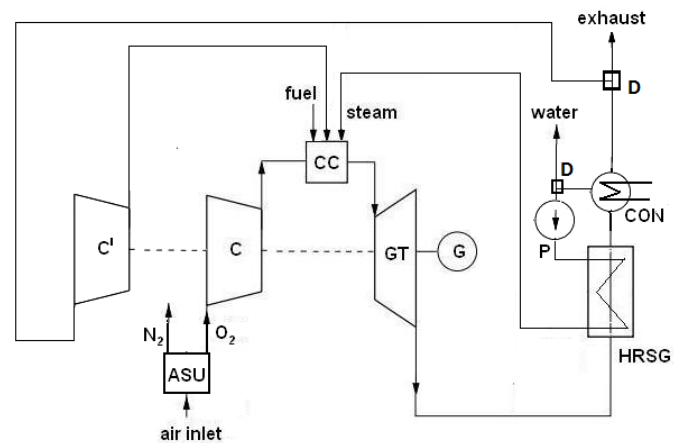


Figure 2. PGE Gorzów plant scheme of a gas-steam turbosets with oxy combustion and flue gases recirculation (ASU - air separation unit, C - compressor, C' - additional compressor, CC - combustion chamber, GT - gas-steam turbine, HRSG - heat recovery steam generator, P - pump, CON - condenser, D - dividing elements).

steam/water injection and steam from exhaust gases condensation (Fig. 1 and Fig. 2). The basic original cycle contains: 12-stage compressor (C); silo-combustion chamber (CC), and three stage gas turbine (GT). Modernized cycle presented on(Fig. 2) contains also; an air separation unit (ASU); heat recovery steam generator (HRSG), condenser of water vapor (CON), additional compressor (C') for recirculation flue gases, a pump (P) and dividing elements (D).

The station ASU products ca. 14,8kgO₂/s and its power consuming ratio is 0,248kWh/kgO₂ [6]. From HRSG one obtains mass flux of steam $\dot{m}_{st}=28\text{kg/s}$, what together with the combustion steam flux (ca. 8kg/s) gives 0,2 mass fraction in steam-gas working fluid. This H₂O - CO₂ mixture expands in a gas turbine from pressure 16,2 bar to ambient pressure, and next, after cooling down in HRSG, goes into a steam condenser. The excess of CO₂ after compressing to the pressure of liquidation is removed from the cycle [6; 7].

Comparison of solutions

The principal differences in both modifications lead on the treatment of amount of injected fuel and amount of components working medium. In the second modification (Fig. 2) the fuel mass flow rates \dot{m}_f becomes the same like in original GT8C. In the first one (Fig. 1), the fuel mass rate becomes higher. We noted that together with increasing of \dot{m}_f the temperature at combustion chamber t_{KS} grow. The netto efficiency of IFFM cycle with oxy combustion and capture CO₂, at the level of $\eta_{el-netto} = 43.67\%$. The decrease of the efficiency is caused by the oxygen producing (6.38%) and capture the CO₂(2.28%). The indubitable advantage of this cycle with oxy combustion and CO₂ capture is lack of pollution such as NO_x and CO₂ (Fig. 2). Essential results are shown in (Tab. 1).

Table 1. Comparison of two conversions of GT8C into the gas-steam turbine.

Parameters	dimension	Original GT8C	I modification Fig1	II modification Fig2
t_{0t}	[°C]	15	15	15
p_{0t}	[bar]	1,013	1,013	1,013
t_f	[°C]	15	15	15
p_f	[bar]	40,5	40,5	40,5
\dot{m}_f	[kg/s]	3,21	12,83	3,41
\dot{m}_{sp}	[kg/s]	182,3	182,3	182,5
\dot{m}_{st}	[kg/s]	-	-	28
t_{st}	[°C]	-	-	580
t_{GT}	[°C]	520	272	591
t_{KS}	[°C]	1100	1274	1032
η_{el}	[%]	34,8	43,66	32,55
N_{el}	[MWe]	54,5	281,3	54,1
\dot{m}_{spot}	[kg/s]	182,3	35,8	11,0
CO ₂	[kg/MWh]	592	0	610
NO _x	[kg/MWh]	0,3670	0,0003	0,0079
[O ₂]	[-]	0,139	0,002	0,181
[H ₂ O]	[-]	0,076	0,001	0,017
[N ₂]	[-]	0,745	0,014	0,027
[CO ₂]	[-]	0,031	0,987	0,775
[NO _x]	[ppm]	30	0,6	15

The electrical efficiency of the conventional GT8C is calculated to be $\eta_{el} = 34,8\%$. The GT8C conversion to the gas-steam cycle with oxy combustion results and recirculation in decreasing of efficiency to the level of $\eta_{el} = 32,6\%$. But simultaneously, the significant decreasing of NO_x emission to the level of

8g/MWh have been observed. Yet other advantage is reduction of the flue gases rates that is rejected into ambient air: 11kg/s, since the flux 136 kg/s flue gases undergo recirculation connected with condensation of 35kg/s steam water. It is also observed the increase of CO₂ emission to ca. 18kg/MWh In comparison with the original cycle GT8C. On the other hand in both modification, simultaneously, the grow of mole fraction [CO₂] from level 0,03 to 0,987 (I modification - CO₂ is captured in the end) to 0,78 (II modification) is observed (Tab. 1). It appears that one obtain the better conditions to carbon capture from the flue gases.

ZERO-EMISSION CYCLE WITH SOFC AND GAS TURBINE

Nano-phenomena within SOFC

Within the context of mounting pressures on zero emission technologies fuel cell systems will play a major role. Since a fuel cell, like SOFC is working without the Carnot limit of efficiency, the systems build on the fuel cells can approach more effective, then conventional, energy conversion processes. On known system combining SOFC and gas turbine working with power 300 kW, has been developed by Siemens Westinghouse. Yet another system leading to advance zero emission power plants has been prepared and tested by Lemański [10]. Their concept is to combine high-temperature solid oxide fuel cells (SOFC) with gas shifting and post-combustion of a rest fuel within a one chamber. Since the efficiency of pSOFC/GT system depends mainly form a level used pressure, Lemański has research a system with double levels of pressure and double SOFC; one working in the higher and one in lower pressure (Fig. 3). The ratio of both pressures change from $\Pi = 1 \div 3.8$ and it depends on additional heat exchange between high and low pressure parts. The electrical efficiency of double pressure pSOFC/GT system is calculated - with increase of Π the electrical efficiency both SOFC becomes lower, but tie total efficiency of system increse mainly due to higher inlet parameters for gas turbine. To be included is delving into the impact fuel cell-CO₂ capture technology from hydrocarbon sources might have in terms of energy economics, as well as on our evolving energy resource mix and on renewable energy development.

CFD simulation

The high temperature solid oxide fuel cell is build mainly from nanomaterials. It consists of two porous electrodes separated by a dense solid electrolyte. Finding of a solid-state material that operate at temperatures as high as 1000°C is a serious challenge. Especially, porous ceramics, being double phase electrodes, needs advanced mathematical modeling [3; 8] which include some nano-flow effects. The phenomenological description of a combination of a huge number of a single nano-channel can be given by two geometrical parameters of porous body: porosity factor, the mean pore radius, and tortuosity. Tortuosity is defined as the ratio of the porous channel length to the straight distance between the end surfaces of the control volume. Tortuosity together with porosity indicates the ratio of the active surface to the volume electrodes. Mean radius of pores is the basic parameter determining nano-flows. All these parameters are involved mainly in description of parameters of 3D model like the diffusive transport of species throughout a fuel cell. The main diffusion mechanism i.e. molecular dif-

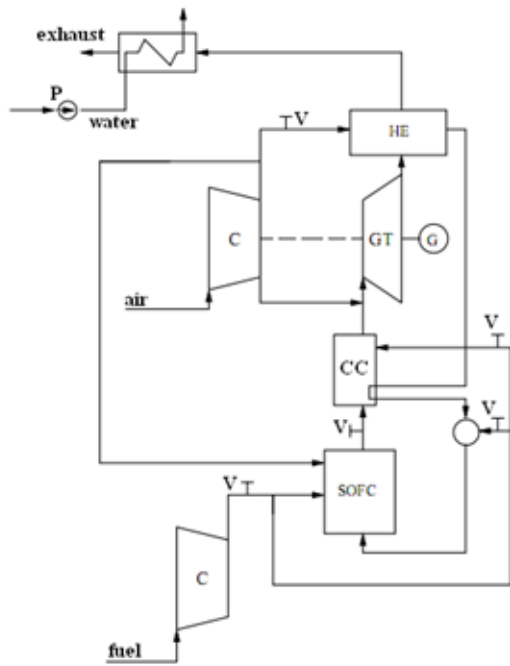


Figure 3. The scheme of hybrid pSOFC/GT used in commercial application by Siemens Westinghouse (SOFC - solid oxide fuel cells, CC - combustion chamber, C - compressor, GT - gas turbine, HE -heat exchanger, V - valve, P - pump) [10; 9].

fusion, Knudsen diffusion and Darcy's pressure diffusion, Pelat electrical diffusion are, generally, a function of above nano-geometrical parameters [2; 3; 1].

On (Fig4) solution domain of a tubular fuel cell is presented. In present paper, a tubular geometry examined by Siemens and Westinghouse was employed with basic dimensions given elsewhere [4]. The model has been implemented into commercial solver using user subroutine technique (UDF) and validated.

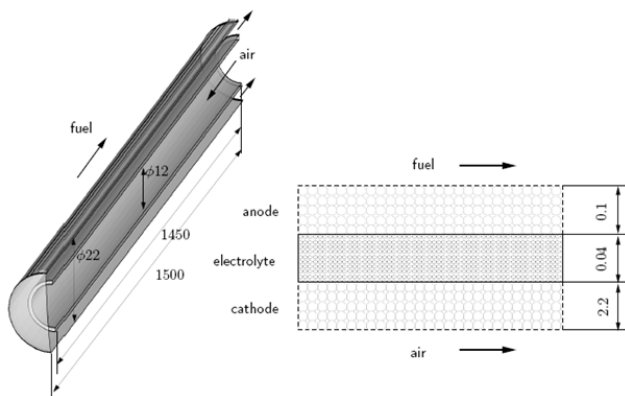


Figure 4. 3D Computational domain for a SOFC tubular [8].

Local solution based on slip velocity, thermal, mass and electric potential mobility forces has been adopted in average manner to transcription of phenomenological coefficients in function of porosity, tortuosity and mean pore size. Finally the mean pore radii has been taken to be equal 300 nm. In Fig5 dependence of generated voltage on current at various porosities are presented. When lower porosities are assumed the concentration polarization is higher. However, a higher tortuosity explicitly disturb the mass diffusion process (Fig6).

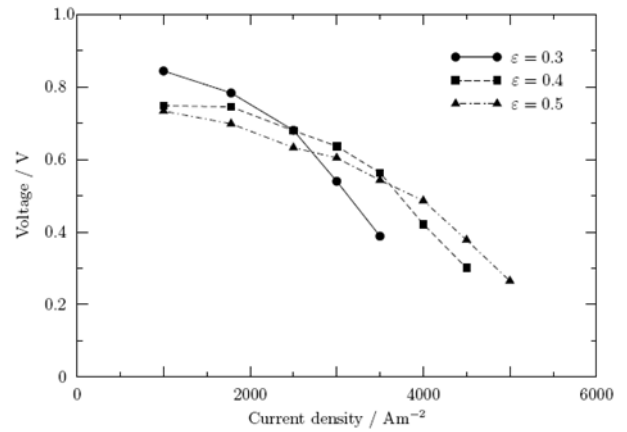


Figure 5. Influence of porosity nano parameter on SOFC performance [8].

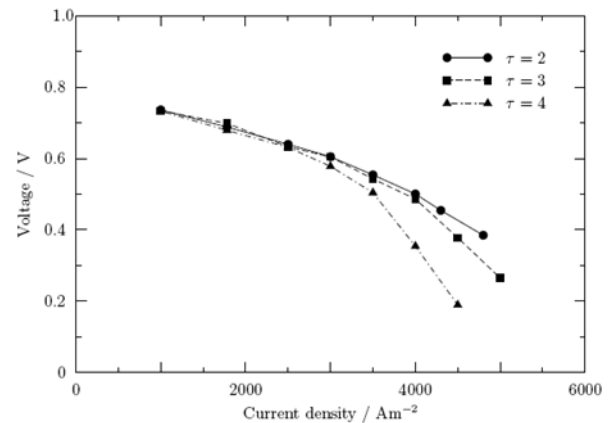


Figure 6. Influence of nano tortuosity parameter on SOFC performance [8].

Yet other novel concept is to use instead of air some oxygen enriched mixture. It can be done if one exchange of ASU unit for oxygen separation by modern technique called the Mixed Conducting Membranes (MCM) which produce pure oxygen from air which produce pure oxygen from air [2]. These membranes acts similarly to the cathode in a SOFC which can conduct ions via non-porous, metallic oxides that operate at high temperatures, i.e. $> 700^{\circ}\text{C}$. In comparison to cathode material it has high oxygen flux and selectivity. Utilization of the MCM reactor instead of ASU means its integration into conventional gas turbine combustion. Similarly to SOFC, the classical chamber in an ordinary gas turbine is replaced by the MCM-reactor, which includes a combustion chamber, a 'low' temperature heat exchanger, an MCM membrane and a high temperature heat exchanger. The concept allows 100% CO_2 capture, increase of cycle efficiency to 50%, and will in this case have less than 1 ppm v/v NO_x in the oxygen depleted outlet air.

ROLE OF NANO-FLOWS PHENOMENA

Despite the achieved fluency in experiment design, there is an apparent lack of understanding of the energy conversion enhancement in it's theoretical background. This is revealed with the numerical prediction discrepancy compared to measurement. Usually, the discrepancy grows with the growth of a medium rarefaction, and the channel hydraulic diameter [2; 3]. That is, when the channel's diameter is comparable with the mean free path of molecules (which is defined as Knudsen

number), acquired either through increased rarefaction or decreased channel diameter, the flow slip seems to occur. This rule also stands for other phenomena, when their influence on the bulk flow is not negligible. By the last statement it is understood, that although the phenomena may be present in a large scaled devices, they seem to be of insignificant importance. When the boundary layer however, extends to the bulk, as it takes place in micro and nano channels, the wall effects alter the entire flow field.

Boundary friction forces

In nano-flow boundary friction appear as a generalization of Young's form of boundary condition:

$$\vec{f} + \vec{\tau}_w = 0. \quad (1)$$

which stay that the boundary friction force is equal to the fluid "wall stress". It is a very neat representation, and to some extent complete. If one considers a simple flow of a fluid in contact with the solid wall we must to add a condition that the solid "wall stress" should be equal the fluid "wall stress" and the friction force. However, in a more general case, as Poisson has shown, the condition requires further extension for the inclusion of capillary forces, most important in case of multi-phase flows. The capillary forces may have a strong influence on friction and velocity slip. The Cauchy boundary condition is hence supplemented with an additional term by Poisson, and has a form:

$$\vec{f} + \vec{\tau}_w + \text{div}_s \left(\gamma \overset{\leftrightarrow}{I}_s \right) = 0 \quad (2)$$

According to Duhem and Roy the friction forces must be based on the velocity slip in the following form :

$$\vec{f} = \left(v_0 \frac{1}{|\vec{v}_s|} + v_1 + v_2 |\vec{v}_s| \right) \vec{v}_s \quad (3)$$

governed by three slip coefficients v_0, v_1, v_2 and where \vec{v}_s - surface velocity. On the other hand, in the boundary condition definition Eq.(1), there is the wall stress vector, which is, in accordance with Cauchy definition, defined to be $\vec{\tau}_w = \overset{\leftrightarrow}{t} \vec{n}$, where $\overset{\leftrightarrow}{t}$ is the Cauchy tensor of momentum flux.

Transpiration effects

Graham and Reynolds transpiration effect manifests itself as a countercurrent at the wall to the main flow. That is, while the gradient between the inlet and the outlet of a microtube generates the flow in the opposite to the gradient direction, the transpiration occurs as the counter flow at the fluid - solid interface. When spoken of Graham observed transpiration, we speak of concentration transpiration. The "wall flow" occurs from the region of a lower concentration to the region of a higher concentration of a given constituent. When spoken of Reynolds observed transpiration, we speak of thermal transpiration, i.e. the flow from region of a lower temperature to the region of a higher temperature, also at the fluid - solid interface. Taking into account the transpiration effects, and also accounting for

the pressure transpiration we achieve a more general form of the friction force definition as:

$$\vec{f} = v_1 (\vec{v}_s - \vec{v}_{wall}) - (c_{s,\varpi} \text{grad}_s \varpi + c_{s,c} \text{grad}_s c + c_{s,\theta} \text{grad}_s \theta + c_{s,\phi} \text{grad}_s \phi) \quad (4)$$

Where appears Navier's slip coefficient and the pressure ($c_{s,\varpi}$), concentration ($c_{s,c}$), thermal transpiration ($c_{s,\theta}$) and electro-mobility $c_{s,\phi}$ coefficients, respectively.

Temperature jump model

Proposed by von Smoluchowski temperature jump model introduces a characteristic length scale It defined as the jump length, which is connected with the heat boundary condition:

$$h(\theta - \theta_{wall}) + \vec{q} \cdot \vec{n} = 0, \quad (5)$$

where heat flux is defined by Fourier law $\vec{q} = \lambda \text{grad} \theta$; h - coefficient of thermal conduction, θ_{wall} - temperature on the wall, λ - thermal conductivity coefficient

Temperature jump length was defined by Smoluchowski to be:

$$l_\theta = \frac{\lambda}{h}. \quad (6)$$

Now if one postulate of Navier-Stokes layer temperature then a generalized form of the boundary condition has a form:

$$\partial_t (c_{p,s} \theta_s) + \text{div} (c_{p,s} \theta_s \vec{v}_{s||}) - \theta_s \overset{\leftrightarrow}{I}_s \vec{v}_s \vec{n} + \text{div}_s (\lambda_s \text{grad}_s \theta_s) + h(\theta - \theta_{wall}) + \vec{q} \cdot \vec{n} = 0 \quad (7)$$

where $\overset{\leftrightarrow}{I}_s = \overset{\leftrightarrow}{I} - \vec{n} \otimes \vec{n}$, \vec{n} - normal vector, γ - surface stress, div_s - surface divergence, grad_s - surface gradient, $c_{p,s}$ - specific heat of thermal layer, θ_s - temperature of thermal layer $\vec{v}_{s||}$ tangent component of \vec{v}_s .

Concentration jump model

In case of the flow of a fluid mixture an effect of concentration jump may occur, particularly when the reactin mixture is considered, and channel walls have catalytic properties. Thus the discontinuity of concentration may take place in the direction normal to the wall. The model proposed by Lewis defines the concentration boundary condition as follows:

$$\alpha(c - c_{wall}) + \vec{j} \cdot \vec{n} = 0, \quad (8)$$

where constituent flux is defined according to Fick diffusion law $\vec{j} = D \text{grad} c$.

The closure for a corresponding concentration jump was proposed in literature, to be defined as:

$$l_c = \frac{D}{\alpha} \approx 0.03 \text{mm}. \quad (9)$$

Postulating the layer concentration the generalized form of the concentration boundary condition is:

$$\partial_t (\rho_s c_s) + \text{div} (\rho_s c_s \vec{v}_{s||}) - c_s \overset{\leftrightarrow}{I}_s \vec{v}_s \vec{n} + \text{div}_s (D_s \text{grad}_s c_s) + \alpha(c - c_{wall}) + \vec{j} \cdot \vec{n} = 0, \quad (10)$$

Electric current jump

Numerous researcher on jonic electric current have been shown [8; 10] that enhancement flow of electricity is observed due to nanostructure of the electrolyte medium. Therefore, according to [8] we propose to replace the classical condition of disappearance of electric current on a boundary $\mathbf{j} \cdot \mathbf{n} = 0$, where the jonic current $\mathbf{j} = \sigma \text{grad} \phi$ is described by the Ohm law based on bulk conductivity constant σ – by the following condition of "electric jump":

$$\mathbf{j} \cdot \mathbf{n} + \text{div}(\sigma_s \text{grad}_s \phi) = 0. \quad (11)$$

The surface gradient of electric potential is very important now. It can be treated as a "mobility" surface force. If this force is added to general friction force (4) some additional surface flow appears which is known to be the Pellat effect.

SUMMARY

In the paper the different effects coming from generalized boundary condition model derived in IFFM PASci has been described and numerically implemented 3D as well 0D model. It was shown, that more than velocity slip may account for the enhanced flow phenomenon, i.e. the concentration, thermal, pressure, electric charge or phase progress may have considerable impact on the flow, efficiency, power performance increase. Aside from co - current and counter - current velocity profile influences observed in the micro and nano flows, there exist phenomena enacting on the temperature or concentration continuity occurring in the temperature and concentration jumps in the normal to the fluid - solid interface direction. These discontinuities are non negligible due to strong wall domination in the micro and nano flows. Further experimental and theoretical investigation in this field is also required to establish the form and value of the model parameters. Along with the mentioned merits, the model provides a good physical interpretation of all the terms, however experimental research is required for further confirmation of the model assumptions.

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