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MISCIBLE DENSITY DRIVEN CONVECTIVE MASS TRANSFER PROCESS ANALYSIS BASED ON ENTRANSY DISSIPATION THEORY

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ABSTRACT
Density driven convective mass transfer process in porous media is one of the most universal phenomena in underground aquifer. In this study, an original model defining Nu (or Sh) number for miscible mass transfer system was derived, based on basic concept of integrated entransy dissipation rate. Numerical simulation results of density driven convective mass transfer process in a closed Hele-Shaw cell and porous media are analyzed. In the process of dilute brine-water mass transfer system in Hele-Shaw cell, three different stages were observed. Meanwhile, time dependent entransy variation and Nu number using our definition also show three different steps in accordance with the observing phenomenon which are perturbation growing stage, instable mass transfer stage and stabilized stage. Very different fingering patterns were observed in dilute brine-water system and PEG-Water system because the latter one has not only the Non-Monotonic Density-Concentration profile but also the strong dependence of viscosity on concentration which can cause viscous-instability accompanied with density driven instability.

INTRODUCTION
Density driven convective mass transfer process is one of the most universal phenomena in underground aquifer. A great deal of study including both experimental and numerical has been developed for its special significance on the transport of containment, seawater intrusion[1] and CO_2 sequestration[2] process. The mass transfer can be enhanced via the density driven instability on account of the dense fluid overlies less-dense fluid and results in more disordered and homogeneous spatial distribution of component in miscible condition or phase in immiscible condition comparing with the stable conditions which can only transport mass by dissolution on the interface and diffusion in the bulk.

To establish a quantitative description of the enhancement caused by the density driven convection, especially for the estimation of CO_2 sequestration security in saline aquifer, several experimental and numerical researches have been developed including both miscible and immiscible system. Kneafsey and Pruess[3] observed immiscible density driven convective mass transfer of CO_2 in aqueous solution in a transparent Hele-Shaw cell and numerical simulation was developed according to the experimental condition as a comparison. The change of so called “affected area” with time was showed as a represent of mass transfer rate for several different experimental conditions, but a rigid non-dimensional number describing the mass transfer rate usually used as Sh (or Nu) was not mentioned. To obtain precise and quantitative description for convective mass transfer rate in the Hele-Shaw cells, Backhaus [4] et al. defined Nusselt (Nu) number for their analysis of the experiments using the Propylene glycol-Water fluid system which is miscible. The definition of Nu was physically explained as the actual mass flux normalized by diffusive mass flux, and the actual convective mass flux also depended on the “area of water consumed” which observed by experimental study similar to the affected area in Kneafsey’s work. More recently, Tsai [5] et al. observed effects of inclining boundary on the density driven mass convection using the Propylene glycol-Water fluid system identical with the work of Backhaus et al, and the transport phenomena was observed not only in Hele-Shaw cell, but also in the particle packing porous media. Similarly, they also defined Nu number using the idea identical to study of Backhaus et al.

Mass flux estimated by the concept of “affected area” in aforementioned studies, provided a way for describe the

speed of mass transfer. But in a closed system with miscible fluid like the Hele-Shaw cells aforementioned, there is no “mass flux” through any physical boundary and the estimation of affected area also needs to define a boundary between water and Propylene glycol which is somehow artificial and non-physical for miscible multi-component fluid system.

To avoid definition of mass flux through a non-physical interface, a new method using integrated entransy dissipation time to define Nu number was put forward in present study. Entransy[6][7] is a physical quantity describing heat transfer capability in terms of the analogy between heat and electrical conduction. Guo and his coworkers derived definition of entransy and used this new concept to optimization of heat transfer process for extensive application cases. Entransy of mass transfer [7] was also derived simply in terms of the similarity of heat and mass transfer governing equation, but only a few publications focused on the application of mass transfer entransy.

In this study, the concept of mass transfer entransy was not used for giving an optimization like previous studies, but for generating a rigid definition of time dedpendent Nu number for miscible fluid convection in a closed system which is difficult to define any flux through a boundary. The Nusselt numbers were calculated based on definition in this study using concept of mass transfer entransy dissipation ratio according to the simulation results. The mass transfer enhancement by the density driven (or natural) convection as a function of time was successfully estimated by the newly defined Nu number.

NOMENCLATURE

A	=	Area of the Boundary
D	=	Diffusivity or Dispersivity tensor
E	=	Entransy or Electronic Energy
Fo	=	Fourier Number
H	=	Height of the Cell
L	=	Characteristic Length
Nu	=	Nusselt number
Q	=	Heat or Mass Flow Rate, Electrical Heating Rate
Ra	=	Rayleigh number
T	=	Temperature
U	=	Superficial Velocity, Electric Potential
a	=	Thermal Diffusivity
c	=	Concentration (mass fraction) or Specific Heat Capacity
h	=	Convective Heat Transfer coefficient
j	=	Current Density
k	=	Permeability
p	=	Pressure
q	=	Heat or Mass Flux
u	=	X Component of Velocity Vector
v	=	Y Component of Velocity Vector

Greek Symbols

λ	=	Thermal Conductivity
μ	=	dynamic viscosity
ν	=	kinematic viscosity
ρ	=	Density
τ	=	Time or Characteristic Time Scale

Subscripts

c	=	Constant
cond	=	Conductive
conv	=	Convective
dis	=	Dissipation
diff	=	Diffusive
eff	=	Effective
mass	=	Mass Transfer
max	=	Maximum
ph	=	Physical
R	=	Resistant

1 Methodology

1.1 Entransy and Entransy dissipation

It is quite common to analog conductive heat transfer problem or diffusive mass transfer problem with electrical conduction problem, due to the similarity of Fourier’s law, Fick’s law and Ohm’s law. According to previous study of Guo et al.[6] , electrical energy stored in the capacitor is corresponding to Entransy which is defined as following equation:

$$E = \sum \frac{1}{2} mcT^2 = \int \frac{1}{2} \rho c T^2 \mathrm{d}V \tag{1}$$

Similar to the energy in electric system, entransy characterizes the capability of heat transfer for a certain object or a system. Meanwhile, like electric energy dissipates when current flows though resistance, entransy also dissipates during heat transfer process. The equation for the rate of electrical energy dissipation can be written as:

$$Q_R = \int \mathbf{j} \bullet \nabla U \mathrm{d}V \tag{2}$$

Similarly, entransy dissipation rate of a heat transfer process also can be written in a analogical way:

$$\dot{E}_{dis} = \int \mathbf{q} \bullet \nabla T \mathrm{d}V \tag{3}$$

where ∇T represents temperature gradient of heat transfer process. The physical meaning of entransy dissipation rate can be explained as capability loss during heat transfer process which is thermodynamically always irreversible.

Based on analogy between mass transfer and transfer processes aforementioned, the entransy and entransy dissipation rate of mass transfer can also be defined as flowing equations:

$$E_{mass} = \int \frac{1}{2} \rho c^2 \mathrm{d}V \tag{4}$$

$$\dot{E}_{mass-dis} = \int \mathbf{q}_{mass} \bullet \nabla c \mathrm{d}V \tag{5}$$

The entransy and dissipation rate of mass transfer also represents the capacity of transfer and its loss corresponding to the mass transfer process of certain component.

The purpose of introducing the concept of entransy and entansy dissipation rate is merely to quantify the speed of

mass or heat transfer and derive a definition of Nu (or Sh) number under the conditions concerned by this work.

1.2 Relationship between entransy dissipation and Nu

For a given system without convective transport of heat or mass through its boundaries, also known as closed system (but not isolated) system in terms of thermodynamics, it is possible to establish a link between entransy dissipation rate for transferred heat or mass and the transfer speed. It is quite obvious that a faster transfer causes higher entransy dissipation rate since the entransy dissipation rate is defined as proportional function of local transfer flux.

To establish the relation of entransy dissiopation rate and Nu number, the physical essence of Nu or Sh number has to be clarified first. Nu number for a convective transfer system can commonly defined as following equation:

$$\mathrm{Nu}=\frac{hL}{\lambda} \tag{6}$$

where, the convective transfer coefficient h defined as:

$$h=\frac{Q}{A\Delta T} \tag{7}$$

Mean while, the characteristic time of conduction process and convection process can be scaled as following:

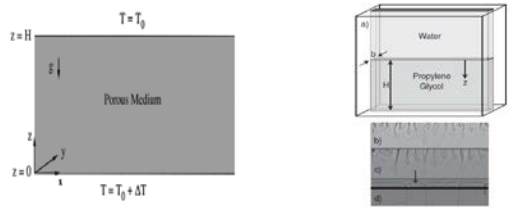
$$\tau_{cond}=\frac{L^2}{a}=\frac{L^2}{\lambda/\rho c} \tag{8}$$

$$\tau_{conv}=\frac{\rho cV\Delta T}{Q}=\frac{\rho cV\Delta T}{hA\Delta T}=\frac{\rho cL}{h} \tag{9}$$

Thus, Nu number can also be treated as the ratio between characteristic time scale of conductive process without flow which is imagined artificially and convective process which is physically happening in fact.

$$\mathrm{Nu}=\frac{\tau_{cond}}{\tau_{conv}} \tag{10}$$

This equation is physically quite making sense that how many times the transfer process has been fastened by convection comparing with pure conductive process. For most condition of heat transfer process the two equations calculating Nu number is equivalent, but it is not always true. According to the traditional definition of Nu number written in the form of equation (6), it is necessary to define a clear boundary of transfer system, so that the heat (or mass) flow rate Q and temperature difference Δ T(or concentration difference Δ c) can be defined. The constraint of 'well defined boundary' is true for most convective heat transfer processes people concern, but still not all of them. Moreover, for most mass transfer process in a closed system, it is difficult to find out a 'boundary' with flux directly as shown in figure 1-B.



(A) Steady state heat transfer (B) Transient mass transfer

Figure 1. Comparison of natural convective common mass and heat transfer system.

To overcome the difficulty, equation (10) can be used as definition of Nu number, but the clear definition of 'time scale' is still needed for further calculation. In this study, we propose a definition of the time scale based on entransy dissipation aforementioned which is the time needed to dissipate a certain amount of entransy in a transfer system.

For example, in the system shown in figure 1-A, if the assumption can be made that there exists another heat transfer system which can only conduct the heat with same conductivity but does not flow, the Nu number of natural convective heat transfer process is often written as following equation:

$$\mathrm{Nu}=\frac{hL}{\lambda}=\frac{q_{conv}}{q_{cond}} \tag{11}$$

According to aforementioned definition, the entransy dissipation rate of this system can be written as following:

$$\dot{E}_{dis}=\int \mathbf{q}\bullet\nabla T\mathrm{d}V=q\Delta T \tag{12}$$

So the Nu number of the natural convection process can also be treated as the ratio of two entransy dissipation rates:

$$\mathrm{Nu}=\frac{q_{conv}}{q_{cond}}=\frac{q_{conv}\Delta T}{q_{cond}\Delta T}=\frac{\dot{E}_{dis\text{-}conv}}{\dot{E}_{dis\text{-}cond}} \tag{13}$$

In other words, the Nu number is also inverse ratio of time needed for dissipating the same total amount of entransy.

$$\mathrm{Nu}=\frac{\tau_{diff}(\Delta E)}{\tau_{conv}(\Delta E)} \tag{14}$$

For the unsteady state mass transfer process shown in figure 1-B, since the 'boundary' is not as clear as heat transfer process in figure 1-A, it is difficult to state the flux q and the convective transfer coefficient h as aforementioned. But there is no special difficulty for calculating the entransy dissipation rate and total entansy dissipation during the process by integration. If the Nu number can be defined as the ratio of time needed in pure diffusive (or conductive) transfer process and convective process for the same total entransy dissipation as shown in equation (15), then a time dependent Nu number can be drawn out for this unsteady convective transfer process without a clear 'boundary'.

$$\mathrm{Nu}\ (\Delta E)=\frac{\tau_{diff}(\Delta E)}{\tau_{conv}(\Delta E)}=\mathrm{Nu}\ (\tau_{conv}) \tag{15}$$

In following sections, this definition of Nu number was applied to analyze the density driven convective mass

transfer process in closed Hele-Shaw cell or porous media using the data from numerical modeling. For mass transfer systems studied in this work, since no mass flowing though physical boundary, the total dissipation of entransy is identical to the total entransy reduction of the entire system. For processing data of numerical modeling, we integrated the total entransy of the system at given moment rather than integrating the entransy dissipation rates since the former is more convenient.

For example, if the total entransy of convective and pure diffusive transfer systems are like shown as in figure 2, the time dependent Nu number can be defined.

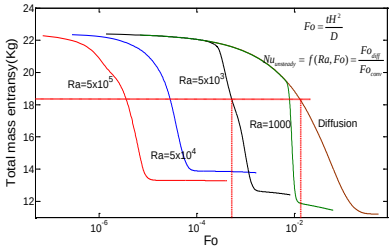


Figure 2.Time dependent total mass entransy of brine-water system.

2 Numerical simulation methods

2.1 Physical model and governing equations

For validating the Nu number definition based on entransy dissipation rate, several numerical simulation cases have been drawn out using commercial CFD program Fluent 13. The governing equations of fluid flow are generalized Darcy-Brinkman 2D Navir-Stokes equations shown as following.

$$\frac{\partial \rho_c}{\partial \tau}+\nabla\bullet(\rho_c U)=0 \tag{16}$$

$$\frac{\partial \rho_c u}{\partial \tau}+\nabla\bullet(\rho_c uU)=-\frac{\partial p}{\partial x}+\nabla\bullet(\mu_{eff}\nabla u)-\frac{\mu}{\mathrm{K}}u$$

$$\frac{\partial \rho_c v}{\partial \tau}+\nabla\bullet(\rho_c vU)=-\frac{\partial p}{\partial y}+\nabla\bullet(\mu_{eff}\nabla v)-\frac{\mu}{\mathrm{K}}v-\rho_{ph}(c)$$

where ρ_c is the reference density of the fluid and $\rho_{ph}(c)$ is concentration dependent physical density (according to Boussinesq assumption), and the effective viscosity of Brinkman term is simplified as equal to bulk viscosity of fluid.

The governing equation of mass transfer is convection-diffusion equation shown in the equation (17) and solved using Fluent user defined scalar.

$$\frac{\partial c}{\partial \tau}+\nabla\bullet(cU)=\nabla\bullet(D\nabla c) \tag{17}$$

The effective diffusivity D is the sum of molecular diffusivity and hydraulic dispersivity if the transfer process happens in the porous media. (Assume that dispersion in Hele-Shaw cell is negligible.)

In the numerical solving process, second order upwind scheme was used as discretization methods of the momentum and concentration equations, and SIMPLE method was applied for pressure-velocity coupling.

The geometry of computational regime is a closed 2D rectangle box with 0.1m length of each side and the grid independency was converged at 400x400 uniform rectangle meshes.

2.2 Rayleigh and Fourier number

In density driven convective mass or heat transfer process (also known as natural convection), Rayleigh number governs the flow. For the bulk fluid, Ra number is defined as follows:

$$\mathrm{Ra}_{\mathrm{bulk}}=\frac{\mathrm{g}\Delta\rho H^3}{\upsilon \mathrm{D}} \tag{18}$$

In porous media, Rayleigh number often defined in an alternative way:

$$\mathrm{Ra}=\frac{\mathrm{g}\Delta\rho kH}{\upsilon \mathrm{D}} \tag{19}$$

Where k is the permeability of the medium, and Rayleigh number defined in this way also known as Rayleigh-Darcy number because it is the product of Darcy number and bulk Rayleigh number. The Ra number mentioned in this study represents the Rayleigh-Darcy number shown in equation (19) unless specifically declared.

The transfer processes concerned in this study are time dependent, so a number to measure the time duration is needed. Here we simply introduce the Fourier number as the dimensionless time:

$$\mathrm{Fo}=\frac{\tau H^2}{\mathrm{D}} \tag{20}$$

3. Results and discussions

3.1 Brine-water mass transfer in Hele-Shaw cell

The concentration dependent physical density of dilute brine (KCl solution) was obtained according to the measurement:

$$\rho_{ph}(c)=\rho_c+6.4233c \tag{21}$$

The simulation cases were started from a initial condition that brine with 3% wt concentration overlying on the top of pure water, and the fluid was assumed to be immobile at the initial moment. The varying Ra numbers were obtained by changing permeability of the Hele-Shaw cells.

Figure 4 shows the concentration distributions of salt at different moments under the condition Ra number equal to 5000. By observing the concentration profiles, three different stages can be found. At beginning, the concentration profile did not show strong convective mixing, but more diffusion like, because there was time needed for perturbation enlargement from a completely static initial condition. And after a while, the convective mass transfer became dominating gradually when the perturbation grow large enough due to the instability. In the end, the heavier fluid went down completely and diffusion dominated the process again.

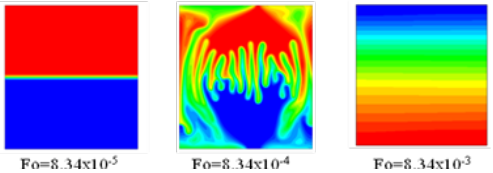


Figure 3.Concentration distribution of brine-water system (Ra=5000)

The curves of simulated total entransy versus time were presented in figure 2. We notice that the curve also showed entransy information about the three stages.

Based on the entransy curve, time dependent Nu numbers were calculated and shown in figure 4. At the first stage which is diffusion dominating, Nu number is around 1. After that, Nu number grows rapidly because the mass transfer has been accelerated by the natural convection. In the end, the transfer process slowed down by stabilization mechanism and Nu number was converging to 1 slowly.

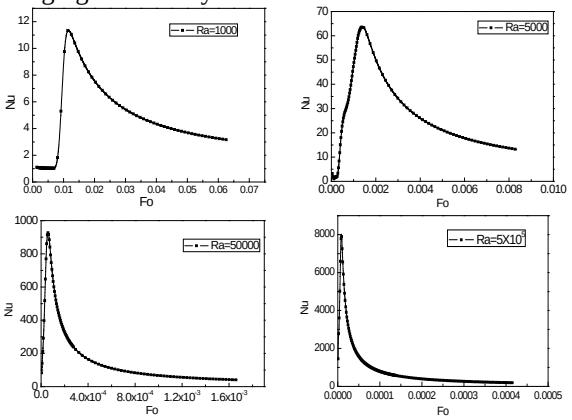


Figure 4.Time dependent Nu numbers under different Ra numbers.

To estimate the effects of Ra number on the mass transfer, the correlation of Nu-Ra has been obtained by Backhaus et al which revealed a power law around 4/5 for a wide range of Ra number. But in this study, one Ra number corresponds to a series of Nu numbers, a number has to be chosen to characterize the mass transfer process. Because the maximum Nu number represents to the acceleration rate at the end of convective mixing stage, the correlation of Nu_{max}-Ra number was obtained in our study. as shown in figure 5.

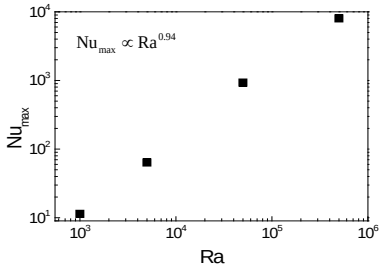


Figure 5. Correlation of Nu_{max}-Ra for brine-water system

3.2 PG-Water mass transfer in Hele-Shaw cell

To analog the condition of CO_2 dissolution in saline aquifer, a series of experimental study has been obtained using propylene glycol (PG)-Water as working fluid. In this work, cases similar to previous experiments have been run. The initial condition of momentum was identical to the Brine case. Pure water was overlying on PG fluid which is heavier, so the system was initially in a stable state. As shown in figure 6, density of mixture reaches the maximum at PG mass fraction around 0.7 and even heavier than pure PG, so the diffusion process can destabilize the system via forming the heavier mixture zone.

The mass fraction dependent properties, including density, diffusivity and viscosity were fitted by polynomial or expotent function. The characteristic density difference in calculation of Rayleigh number was valued by the difference between maximum mixture density and pure PG density. The characteristic diffusivity and viscosity were also valued at the mass fraction corresponding to maximum density.

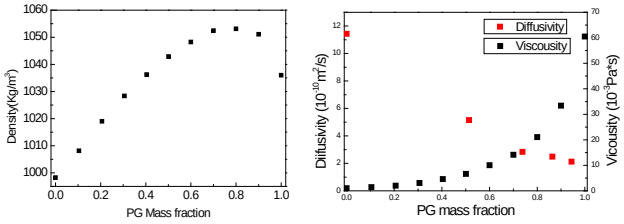


Figure 6. Property of PG-water mixture

The mass fraction distributions at different moments were presented in figure 7 corrensponding to condition which Ra=5000.

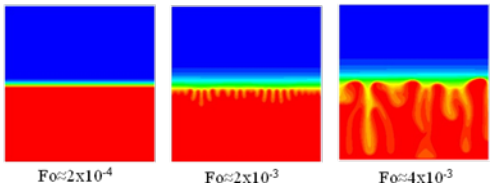


Figure 7. Concentration distribution of PG-water system in Hele-Shaw (Ra=5000)

Very different fingering patterns were observed in dilute PG-Water system and brine-water system because the PG-water mixture has not only the non-monotonic density-mass fraction profile but also the strong dependence of viscosity on mass fraction which can cause viscous-instability accompanied with density driven instability. The longer perturbation growth time than the brine case under the same Ra number was also observed.

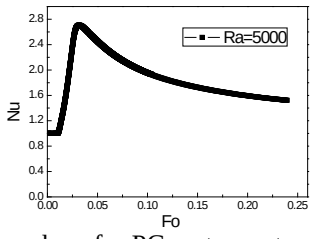


Figure 8. Nu numbers for PG-water system in Hele-Shaw cell (Ra=5000)

Figure 8 showed the Nusselt number corresponding to 5000 Rayleigh number. A much slower mass transfer rate than that in the brine-water case under the same Ra number was observed, and it is consistent with what observed from the mass fraction distribution maps.

The reason causing the slower mass transfer rates observed and one order of magnitude lower Nu number is possibly to be non-monotonic density-mass fraction profile, variable viscosity and diffusivity of fluid, and

therefore, totally different physical meaning of Rayleigh and Fourier number despite of the identical shape of the formula. But after all, the definition of Nusselt number proposed in this paper is still physically meaningful, which showed lower value when the mass transfer is slower.

3.3 PG-Water mass transfer in porous media

The mass transfer phenomena PG-Water mixture in porous media was also observed and compared with the condition which in the Hele-Shaw cell. The boundary and initial settings of the numerical cases are generally similar with the settings Hele-Shaw, but the only difference is the formula of effective diffusivity D. In the porous media, the hydraulic dispersion is not negligible in most situations. The effective dispersivity is tensor included both the effects of molecular diffusion and dynamic dispersion, and the longitudinal and transverse dispersion length was set as 1mm and 0.1mm.

The characteristic diffusivity for calculating the Ra and Fo number was valued identical to the PG-Water Hele-Shaw case described in section 2.4 considered molecular diffusion effect only.

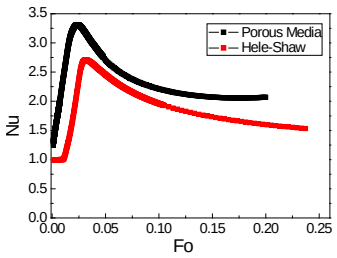


Figure 9.Nu numbers for PG-water system in porous media and Hele-Shaw cell (Ra=5000)

The time dependent Nusselt number was obtained using the entransy dissipation time aforementioned, and compared with the Nu number in Hele-Shaw cell obtained in section 2.4 under the condition Rayleigh number equal to 5000. A slightly higher Nusselt number in porous media was observed due to the additional mass transfer acceleration by the hydraulic dispersion mechanism.

CONCLUSIONS

A new method based on entransy dissipation to evaluate the density driven convective mass transfer enhancement has been developed in this study.

Three different stages of convective transfer process were observed. Mean while, time dependent entransy variation and Nu number using our definition also shows three different steps in accordance with the observing which are perturbation growing stage, instable mass transfer stage and stabilized stage. The Nu number in first stage is around 1 which means the mass transfer rate was not deviated much from diffusion process.

The maximum Nusselt number corresponding to the ending of convective mixing was correlated to Ra number for brine-water system and showed a power law around 0.94 according to our simulation results.

Mass transfer of PG-water mixture was also observed both in Hele-Shaw cell and porous media at Ra number equal to 5000. Much slower mixing rate and lower Nu number was observed due to the complex density, viscosity and diffusivity profile of mixture fluid. A slightly higher Nu number in porous media than that in the Hele-Shaw cell was also observed due to the mass transfer acceleration by hydraulic dispersion mechanism.

ACKNOWLEDGEMENT

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