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TIME SCALES OF PHYSICO-CHEMICALY DRIVEN PROCESSES IN DESULPHURIZATION CaO-Al_2O_3 SLAG

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ABSTRACT

The paper is dealing with the expression of times scales associated to different physically and physico-chemically driven processes taking place on the slag side of the interface CaO-Al_2O_3 slags-steel, specific to the steel refining process. The driving process is that presenting the shortest time scale in comparable conditions with others. The time scale of the main physico-chemically driven process at interface steel-slag, on the slag side serves to evaluate the local interfacial flow. In this paper the conditions to evaluate the time scales are connected to the characteristic length scale of solutocapillarity effect in the form of Marangoni convection which results to be the faster process at the specified length scale taken into account, over the critical values of the solutal parameters, called threshold values.

KEYWORDS: physico-chemically driven process, time scale, solutocapillarity, characteristic length, Marangoni effect.

1. General aspects

Flow phenomena are present and they are of outmost importance in many individual and unitary metallurgical processes. Interfacial flow contributes to the adequate evolution of many refining processes such as non-metallic inclusions removal from metallic melts, gaseous bubbles formation and floating, mass transfer at interfaces between metallic melts and slag (or fluxes). In accordance with the advanced trends in science and technology, aspects concerning the occurrence, evolution, efficiency and mastering of the flow phenomena to achieve a high quality melts must be better analyzed at micrometers and even at nanometers scales. It is also broadly recognized the effect of temperature and of the surface active solutes on the surface and interfacial tensions in both fluids at interface and the adjacent flow phenomena, mainly on occurrence of the Marangoni effects [1] consisting in flow and convection. In order to state the problem of a certain type of interfacial flow an adequate set of dimensionless criteria and the specific time scale must be used. In metallurgical refining systems solutal effects, further called also as solutocapillary effect or solutocapillarity, are predominant compared to other aspects of capillarity. Even the electrocapillarity, which is supposed (considered) to be stronger than the solutocapillarity, originates in the presence and concentration of surface active ionic species. The high values of the thermal conductive coefficient in liquid metals contribute to this particularity, making the thermocapillarity without significance in liquid metal and slag layers even at high values of their depths. The Marangoni solutal effect acts at macroscale, by imposing gradients of concentration through external actions, or at microscale when local gradients of concentration appear due to local inhomogeneities of different origins, along the interface or across it. The actions of different physical and physico-chemical factors as gravity, diffusion/viscosity (called also viscous diffusion), surface tension and solutocapillarity are competing according to their time scales. If the thermal equilibrium in the system steel-slag is considered and the electrical phenomena at interface are neglected, the instability/stability at the interface on the slag side is determined by the competition between the actions of different physical and physico-chemical factors as gravity, diffusion/viscosity surface tension and capillarity. The solutocapillarity is the driving process among different actions affecting the stability in interfacial flow when there are accomplished its conditions of prevalence.

2. Time scale significance

An adequate time scale reflects the dynamics of physical process taken into account and serves to a correct establishing of the time–step size for a numerical simulation of the dynamics.

The representative physical time scales must be adequate to the specificity of the considered problem, evaluated by the typical physical or physico-chemical phenomena such as are gravity, viscosity, diffusion and capillarity, this last the most broad sense. Excepting gravity, these phenomena originate in the complex manifestation of the properties of matter mainly influenced by temperature and chemical composition and these last contribute to them in the form of the thermodynamic and transport properties of the liquid phases. Certain solutes like oxygen and sulphur act simultaneously in systems steel-slag on viscosity, diffusion and capillarity of both mentioned fluid phases. This influence must be evaluated in the complex situation consisting in the simultaneous presence of the above mentioned situation which practically consists in a competition between them to exert the main influence.

If the length scale of the analyzed problem is generically noted *L*, there will be several ways to define it.

Firstly, the length scale is linked to the space extend where the analyzed phenomenon acts and where the phenomenological and quantitative analysis of flow is performed. Then, there are cases where the length scale results from conditions of prevalence of a certain phenomenon compared to another, or of many several phenomena, acting simultaneously.

A phenomenon is characterized by a characteristic time scale resulting from the condition that all physical and physico-chemical effects, reflected by their relevant quantities, counterbalance between them. In this case an adequate selected dimensionless group will have the value equal to unity.

In principle, the time scale associated with the considered driven physical process must be understood as an interval of time of a specific order of magnitude, where the respectively considered phenomenon or effect is the relevant physical phenomenon, presenting the maximal probability to take place, compared with another or several present phenomenon also.

From this point of view there is a certain similitude to the constructal theory and perhaps it may be a way to approach and explore new facets of the behavior of flow phenomena at interface.The point of view of the author of the present paper is that there is a strong similitude with other observed situations at different scales. Until an evaluation is performed on these aspects, it appears as being of outmost importance the establishing of smallest scale of the system, including the time scale, because the competition between the competing processes takes place locally, in determined intervals of time where different variable conditions appear.

3. Characteristic time scales associated to various kinds of physically and physico-chemically driven processes

3.1. Characteristic time scale of gravity driven physical process, (τ_g)

On Earth gravity acts unidirectionally upon the normal direction to the Earth surface and directed to center of the Earth core. Therefore gravity–driven physical process is analyzed always as 1-D problem. The dimensionless Froude number[2] is adequate to characterize the gravity phenomenon:

$$Fr = \frac{inertial\,force}{gravitational\,force} = V_{(g)}^{2} \cdot (g \cdot L)^{-1}$$

where: *g* - is the magnitude of the gravity acceleration; $V_{(g)}$ - is the characteristic scale of velocity; *L* - is the length scale of the considered problem or the characteristic length of the system were the gravity is considered.

The time scale associated with the gravity driven physical process is noted τ_g and it must be understood as an interval of time of a specific order of magnitude, where the gravity is the relevant physical phenomenon. The characteristic scale of velocity $V_{(g)}$, acting on the length scale *L* of the analyzed problem is:

$$V_{(g)} = L / \tau_g$$

Imposing the Froude dimensionless number to be of unity order:

$$Fr = V_{(g)}^{2} \cdot (g \cdot L)^{-1} \approx 1$$

and replacing the relation giving the characteristic scale of velocity given by the relation

( ), the time scale of the gravity driven process is given by the following relation:

$$\tau_g \approx (L/g)^{1/2}$$

3.2. Characteristic time scale of viscous-diffusion driven physical process

There are specific situations including cases in liquid steel refining processes when only viscosity-driven physical process is the relevant process in fluid flow. As an example, the case of steel flow around a solid and non-reactive, non-metallic inclusion which is very stable from chemical point of view, could be considered. Also, cases referring to the rising in steel of gas bubbles of different origins or produced using different devices are considered.

In the cases of pure viscous flow, an adequate dimensionless number is the Roshko number [3] which is the product of dimensionless Strouhal number (*St*) [4] [5] and dimensionless Reynolds number (*Re*) [5]. *St* number is used in the study of periodic or quasiperiodic variations in the wake of objects immersed in a fluid stream. The Strouhal Number can be important when analyzing unsteady, oscillating flow problems. The Strouhal number represents a measure of the ratio of inertial forces due to the unsteadiness of the flow or local acceleration to the inertial forces due to changes in velocity from one point to another in the flow field. It is a dimensionless number describing oscillating flow mechanisms.

The *St* number is often given as:

$St= \omega \cdot L \cdot V^{1}$

Ro number is given by the relation:

$Ro=St \cdot Re=\cdot\ \omega \cdot L^2 \cdot v= \omega \cdot L^2 \cdot \rho \cdot v^{-1}$

In both numbers: ω - is the frequency of vortex shedding; L - is the characteristic length; V - is the velocity of the fluid; ρ - density of the fluid; v - kinematic viscosity of the fluid.

The use of the *Ro* number instead of the *St* number allows to avoid the main uncertainty due to the determination of the velocity *V*.

In specified conditions these dimensionless numbers make possible to evaluate the development of turbulent wakes from vortex streets. At *Re*=40-150, called stable range, regular vortex streets are formed and no turbulent motion at macroscale is developed. In the stable range the vortices decay by viscous diffusion. At *Re*=150-300 it follows a transition of flow to a regime called irregular range in which turbulent velocity fluctuations accompany the periodic formation of vortices. Further, at higher values of *Re* number it follows the fully turbulent flow.

Therefore the time scaling must be performed in different ways. Of a special interest are the stable regime, including the region of very low Reynolds numbers and the transition regime.

3.2.1. Characteristic time scale in the macroscopic stable regime (viscous diffusion)

3.2.1.1. Characteristic time scale at low values of Reynolds number

At enough low values of the *Re* number (<40), the diffusive-viscosity time scale (τ^2_{diff}) results from combining the simultaneous effects of diffusion and of viscosity and it results from the following relation:

$\tau^2_{diff}=\tau_{diff} \cdot \tau_{visc}=(L^2/D)(L^2/v)=L^4/v \cdot D$

where: L - is the characteristic length; D - mass diffusion coefficient of the chemical element able to influence the properties of the interface of the system and thus to act on flow; v - kinematic viscosity of the fluid.

Many times it is considered that what happens at a macroscopic scale it happens also at a microscopic scale and in consequence also at a local scale. Therefore also this regime must be taken into consideration as a competing one against the others.

The relation between the effects of mass diffusion and of the momentum diffusivity is given by the dimensionless Schmidt number *Sc*, expressing the ratio between mass diffusion relaxation time and the viscous time:

$Sc= \tau_{diff}/\ \tau_{visc}= v/D$

3.2.1.2 Characteristic time scale at values 40<Re<150

In this range, of values vortex street patterns appear [6], frequently called stable von Kármán streets; they are classically regular, stable and well defined for long distances downstream. This aspect of flow also appears at higher values of Reynolds number, up to Re≈10^5 and higher, but the free vortices moving downstream are dumped by the turbulent diffusion and the flow aspect turns into turbulent wakes.

3.2.1.3. Characteristic time scale in the transition regime (Re=150-300)

The value of Ro dimensionless number is correlated with the values of the Re dimensionless number [6]:

$R_o= -3.6 \cdot 10^{-4}\ Re^2 +0.391\ Re -48.2$ established for Re=260-350 and R_o=34-44.

Another relation, established for Re=50-180 is the following:

$R_o=0.212\ (Re - 21.2)$

The condition R_o>0 obtained by extrapolation of the first relation gives the value Re> 142. At Re=150 the value R_o=2.35 is obtained, which seems to be consistent with the minimal experimental pair data Re=260; R_o=34. Replacing $f= 1/\tau_{Ro}$ in Roshko number and making R_o=1 the following relation is obtained:

$R_o=L^2 \cdot \rho \cdot v^{-1} \cdot \tau_{Ro}^{-1} =1$

$\tau_{Ro}= L^2 \cdot \rho \cdot v^{-1}$

3.3.Characteristic time scale of surface tension-driven physical process (τ_{Ca})

In viscous flow the surface tension phenomenon is characterized by the capillary number *Ca* [1], frequently called the crispation number *Cr*:

$Ca=\mu \cdot D \cdot \sigma^{-1} \cdot L^{-1}=\mu \cdot V_{(Ca)} \cdot \sigma^{-1}$

where: μ - is the dynamic viscosity; D - mass diffusion coefficient of the chemical element; σ – is the surface tension of the slag; L - is the characteristic length; $V_{(Ca)}$ - is the characteristic scale of velocity in surface driven physical process.

If τ_{Ca} is the typical time scale of the surface driven process then:

$V_{(ca)}=D/L= L/\ \tau_{Ca}$

Imposing the capillary dimensionless number to be of unity order:

$Ca=\mu\cdot V_{(Ca)}\cdot\sigma^{-1}\approx 1$

and replacing the relation giving the characteristic scale of velocity $V_{(ca)}$, the time scale of the surface tension-driven process is given by the following relation:

$\tau_{Ca}\approx L\cdot \mu\cdot \sigma^{-1}$

3.4. Characteristic time scale of solutocapillarity

The variations of the chemical compositions of the slag and steel at interface, due to the mass transfer of the surface active elements as sulphur and oxygen, locally affect the interfacial tension.

In the most frequent situations, due to the actions of many factors the surface tension of liquid phases and in a larger sense the interfacial tension liquid-liquid is not a constant one, mainly due to the specific chemical reactions. It is case of interfaces liquid-liquid (steel-slag, steel-liquid inclusion), liquid-solid (steel-solid inclusion), liquid-gaze (steel-bubble of gaze). In such cases the surface tension presents important variations on local small scale for a certain interval of time, because the re-equilibration of the interface is not an instantaneous one. In the system of two immiscible fluids, separated on the vertical direction according to the difference of density, there are several kinds of gradients of the superficial tension upon the factors affecting this quantity and this is expressed in the global relation (1) for the 1-D case:

$$\tau_S=\frac{d\gamma(c,T,\psi)}{dx}=\frac{\partial\gamma}{\partial c}\frac{dc}{dx}+\frac{\partial\gamma}{\partial T}\frac{dT}{dx}+\frac{\partial\gamma}{\partial\psi}\frac{d\psi}{dx}$$

where: γ is superficial tension of the fluid taken into consideration, or interfacial tension; c – concentration of the superficial active element; T – temperature; Ψ – electric potential, existing or applied; x – direction on which the respective gradient of the superficial tension (or the surface tension) gradient acts, being estimated or computed.

The contribution of the temperature gradient could be considered closed to zero because of the high values of the thermal coefficient in liquid steel which affects also the slag layer in the neighboring zone at interface.

When the dynamic effects induced by solutocapillary effects is analyzed, mainly at a local scale, it is necessary to evaluate first the conditions when the shortest time scale is that of solutocapillarity, when many competing actions are present. If these conditions are accomplished the overcoming of the neutral stability conditions takes place.

In this case, overcoming of a threshold value of the surface active solute concentration leads to the appearance of hydrodynamic instability of the interface, on short scale and on long-scale, caused by the surface tension gradients (the Marangoni effect) of solutal origin. The solutocapillarity is a factor of instability while the viscosity/diffusion and gravity act as stabilizing factors by damping the effects of this instability. Diffusion acts to dampen the concentration fluctuations and the associate fluid flow either along surface or across it, because the directionality of diffusion depends only on the concentration gradient which is a vector. Viscosity acts to dissipate in bulk the kinetic energy of flow.

The gravity acts physically to flatten the interface and thus to stabilize the deformational perturbations. All these actions are competing and the dominating action in this competition is the one having the shortest time scale. This instability presents different convective patterns as regular convective structures (rolls, hexagons), interfacial waves and chaotic convective motions in the vicinity of the interface, called also interfacial turbulence.

It is remarked that the short scale of solutal capillary effects, in the form of local Marangoni flow and adjacent convection contribute to accelerating the interfacial mass transfer which interests in different steel refining processes.

The dimensionless Marangoni number for the solutal case represents the ratio between the destabilizing driving force F_m due to the surface tension gradient and the resistive force F_f due to viscosity/diffusion which is opposed to the first; for the solutal case the following relation for the dimensionless number Marangoni was adapted [1]:

$$Ma_{sol}=\frac{F_m}{F_f}=\frac{\frac{\partial\sigma}{\partial C}\cdot\Delta C\cdot L}{\mu\cdot D}$$

where: $\frac{\partial\sigma}{\partial c}$ – the surface tension coefficient, related to the concentration of the considered surface active element, usually in $N\cdot m^{-1}\cdot(mass\%)^{-1}$; Δc – the surface concentration difference of the considered surface active element, in mole, molar fraction (X) or mass percentage(%mass) between two points separated by the distance L; L – the characteristic length of the Marangoni effect, in meter (m); μ – the dynamic viscosity of the considered fluid,

in $kg\cdot m^{-1}\cdot s^{1}$; D – the diffusion coefficient of the surface active element in the considered liquid, in $m^2\cdot s$.

The flow is destabilized when $F_d>F_f$,i.e when Ma>1. Experimentally, the critical value of the dimensionless Marangoni number is Ma_c= 80. Taken into consideration that $\mu=\rho\cdot\nu$, the Marangoni time scale results in the form:

$$\tau_{Ma} = \left(\frac{\rho \cdot L^2}{\frac{\partial \sigma}{\partial c} \cdot \frac{\Delta c}{L}} \right)^{1/2} = \left(\rho \cdot L^3 / \left(\frac{\partial \sigma}{\partial c} \right) \cdot \Delta c \right)^{1/2}$$

The solutocapillary effects are physically present in a sensitive manner when the conditions are accomplished, i.e. when Ma>Ma$_c$, and in this conditions the equivalent time scale is designed by

$$\tau_{solutocap}\text{, where } \frac{\partial \sigma}{\partial c} \cdot \Delta c > \left(\frac{\partial \sigma}{\partial c} \cdot \Delta c \right)_{crit.}.$$

For the critical value of the dimensionless number Marangoni for the solutal case, a critical value of the time scale is obtained [1]:

$$(\tau_{Ma})_{crit.} = \left(\frac{\tau_{diff} \cdot \tau_{visc}}{Ma_c} \right)^{1/2}$$

4. Comparison between time scales of different physico-chemical actions in liquid steel and slags

A major interest for these aspects is in the field of steel refining under slags.

The case of low carbon aluminium killed steel (LCAK) and desulphurization slags in the CaO-Al$_2$O$_3$system at the temperature of 1873K will be considered, because it influences in many ways the purity of the steel, due to the dynamics of the interface. The data taken into consideration are shown in the table1.

Table 1. *Physico-chemical data and time scale of several physico-chemical driven process in CaO-Al$_2$O$_3$ slags at temperature of 1873K*

Quantity, symbol, units	Values, references	
	Slag 50% CaO+50% Al$_2$O$_3$	Slag 60% CaO+40% Al$_2$O$_3$
Density, ρ, kg·m^{-3}	2710 [10]	2685 [7]
Dynamic viscosity, μ, Pa·s	0.23 [9]	0.1184 [9]
Diffusion coefficient of sulphur, D$_S$, m^2·s^{-1}	$2.48 \cdot 10^{-10}$ [10]	
Surface tension upon the sulphur content (S, mass%), σ, 10^{-3}N·m^{-1}	$1.4781(\%S)^2-22.159(\%S)+546$	$2.1217(\%S)^2-22.922(\%S)+563$
Time scale of the gravity driven process, τ_g, s	$\sim 0.32L^{1/2}$	
Time scale of the mass diffusion driven process, τ_{diff}, s	$\sim 4.03 \cdot 10^9 L^2$	
Time scale of the viscosity driven process, τ_{visc}, s;*Sc* value	$1.178 \cdot 10^4 L^2$; $Sc=3.42 \cdot 10^5$	$2.26 \cdot 10^4 L^2$; $Sc=1.78 \cdot 10^5$
Time scale of the viscous diffusion driven process (*Re<40),* $\tau_{visc.diff}$, s	$\sim 8.47 \cdot 10^6 L^2$	$\sim 9.54 \cdot 10^6 L^2$
Time scale in the transition regime (stable vortex streets) (*Re*=150-300), τ_{Ro}, s	$\sim 3.193 \cdot 10^7 L^2$	$\sim 6.889 \cdot 10^7 L^2$
Time scale of the surface tension driven process, τ_{Ca}, s	$0.23 \cdot L \cdot \sigma^{-1}$	$0.1184 \cdot L \cdot \sigma^{-1}$
Time scale of solutocapillarity, $\tau_{solutocap}$, s Time scale for Ma$_c$, $(\tau_{Ma})_{crit}$, s	$2710 \cdot L^3 \cdot \left(\frac{\partial \sigma}{\partial c} \cdot \Delta c \right)^{1/2}$ $8.613 \cdot 10^2 \cdot L^2$	$2685 \cdot L^3 \cdot \left(\frac{\partial \sigma}{\partial c} \cdot \Delta c \right)^{1/2}$ $1.067 \cdot 10^2 \cdot L^2$

5. Commentaries and conclusions

The analysis of the relations giving the time scales of different physico-chemically driven processes are dependent upon the reference length scale. As it is known the physico-chemical processes take place simultaneously but according to their time scale and at different lengths. Like the time scales, the length scales presents specific values called characteristic scales. The importance of the length scale results from the value of its power in the established expressions. The greater the exponent value, the greater the effect at small values of considered length *L*, in minimizing the time scale of the respective physico-chemical action. This length scale *L* cannot be however too much. For example a limit for the surface tension physically-driven process could be the characteristic length L_c, given by the relation:

$L_c=(\sigma/\rho \cdot g)^{1/2}$

In the considered cases in slags, values of L_c are around 4.5 mm but this is less significance for the solutocapillary effect where the characteristic length scale is about 50-300μm in CaO-Al$_2$O$_3$ slags. At these values of the length scales the shorter time scale results for the solutocapillarity action because of the factor L^3. At the same value of the length scale *L*, lets say 100μm, the following order relation results between the time scales of the considered physico-chemical –driven actions:

$$\tau_{diff} > \tau_{visc.diff} > \tau_g > \tau_{visc} > \tau_{Ro} > (\tau_{Ma})_{crit}, \approx \tau_{ca}$$

In the mentioned conditions it is expected that solutocapillarity should play a major role in the local interfacial dynamics at micrometric scale. At values of the product

$$\left(\frac{\partial \sigma}{\partial c} \cdot \Delta c\right)^{1/2} > \left(\frac{\partial \sigma}{\partial c} \cdot \Delta c\right)^{1/2}_{crit}$$

the value of the time scale τ_{Ma} decreases below the critical value $(\tau_{Ma})_{crit}$ and in consequence the solutocapillary–driven processes (the direct effects and the connected processes) are faster.

The problems of stability around and over these values, called threshold values of parameters, need a separate and special treatment, in specific conditions.

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