

POSSIBILITIES TO EVALUATE THE VALUE OF THE MARANGONI EFFECT AND OF THE MARANGONI NUMBER IN REFINING STEEL-SLAG/INCLUSION SYSTEMS

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ABSTRACT

Starting from the impressive progress in studying the instabilities induced by capillary effects in systems of two immiscible fluids in chemistry, an analysis of factors in solutal Marangoni effect and Marangoni number is performed, regarding the liquid steel surface as a part of the interface in systems steel-slag/inclusion. Low alloyed, microalloyed and carbon steel are taken into consideration because of their closed behavior to liquid iron solutions. Computing relations of surface tension of solutions Fe-O-S and interface tension between the same solutions and Al₂O₃ inclusion, also of the diffusion coefficients of the solutes are proposed to be used in computing the contribution of solutal effects in Marangoni effect and Marangoni number.

KEYWORDS: Marangoni effect, Marangoni number, surface tension, oxygen, sulphur.

1. Introduction

"The mechanical properties of the interface layer between two fluids, including the equilibrium shape of the surface, may be calculated by applying the standard mathematics techniques of mechanics to the forces associated with the surface tension" is formulated in the IUPAC as definition of the subject of capillarity [1].

In the recent decades of years this definition was enriched by a huge amount of scientific research concerning the intimated aspects of capillarity and its implication in clarifying mechanisms of processes involved in current and advanced technologies, at industrial scales and at micro and nanoscale. Many achievements, obtained in the research at micro and nanoscale are of a full utility in explaining many processes at industrial scale in steel refining, serving as a good base for developing new ways of improving the performance and in developing new intelligent devices to control some specific working parameters.

The following survey of adequate found published papers helps in understanding of the achieved knowledge in similar systems in chemistry engineering, used after in bringing a contribution in the attempt to promote a similar treatment, in steel refining metallurgy, based on treatments using slag.

The systems liquid steel-slag and more generally, liquid metals (or alloys)-slag, are systems of two immiscible fluids, because of the differences

as physical and chemical nature of the component fluids, but their evolutions, during the industrial processes, take place mainly by reactions and mass exchange between them, at interface. Thermal flux and the exothermicity of some reactions, taking place during refining treatments of steels using slag, are also to be taken into consideration in a more quantitative manner. Binary liquid-liquid and gas-liquid systems, where an interfacial chemical reaction take place, have been intensively and broadly studied and investigated, especially in chemical engineering, to clarify the interaction between reaction-diffusion phenomena and pure hydrodynamic instabilities.

Liquid steels and the refining slag are not at all simply liquids, they are complex liquid solution of totally different nature as bonding between component species, these also themselves different in the two solutions. This reality, of nature to produce many complications in analyzing the proposed aspects, without any doubt is an argument to sustain once more, if it would be necessary, that in systems steel -slag, the role of the capillary effects is of outmost importance and they merit more than to be simply declared. The difficulty to observe in situ how the phenomena proceed, due to the high temperature around of 1873K, obliges to a careful analysis of other chemical systems of immiscible solutions but direct accessible as observation and measurements, due to their near room temperature or not too different to these values.

2. Aspects of hydrodynamics and capillarity at interface between immiscible fluids

Hydrodynamic instability of the fluid interface may induce local convective fluxes and by these, it affects, in an important manner, the reaction, the interface heat and mass transfers. In these cases, self organization processes may lead to a specific dissipation pattern formation of chemo-hydrodynamic nature [2].

Experimental evidence in liquid-liquid systems of interfacial convection exhibiting a high degree of ordering or interfacial turbulence, when mass transfer is accompanied by chemical reaction, has been reported in the literature for reactions of different types. Among the first descriptions such phenomena is that in the paper [3] where was reported a spontaneous emulsification at the contact between solution of lauric acid in oil and an aqueous solution of NaOH. A spontaneous turbulence and acceleration of the interfacial reaction by convection was observed during the extraction of acetic acid from an organic solvent into an alkaline solution [3]. The interfacial turbulence was reported as taking place when a reaction take place at an oil-aqueous interface [4]-[6][9]. Many data, concerning the spontaneous turbulence, also are reported in a wide range of other activities, such as in nuclear fuel reprocessing activities [7] or at liquid-gas interfaces driven by photochemical reactions [8]. Aspects of interfacial interfacial instabilities were observed during the extraction of uranyl nitrate from its nitric acid solution. Another example was given in paper [8], where was studied the pattern formation. In [9] are presented the dynamics of chemically driven nonlinear waves and oscillations at an oil-water interface.

Phenomena attributed to heat and solutal effects due to an exothermic neutralization reaction interplaying with a liquid-liquid interface and convection, observed experimentally, are reported in the paper [10] and are characterized by the authors as a novel instability, occurring when an organic solution, containing an acid, is in contact with an aqueous solution in which NaOH is dissolved. It was suggested that the self-sustained dynamics and pattern formation, in the form of plumes and fingers are produced because of the coupling between different hydrodynamic instabilities; boundary layer and double diffusion instabilities are mainly involved. When in the same system NaOH was replaced by an organic base it was observed a regular structure, in the form of long self-growing cells, with one side keeping contact with the interface and the other side propagating in the direction out of the interface [11]. According to these cited papers, several mechanisms of instability, like surface tension driven

or buoyancy driven, may compete. Replacement of NaOH anorganic base by an organic base has produced the increase of the influence of the Marangoni effects probably because of increasing of the chain length of the new resulting salt. Similar aspects to those before mentioned are presented also in papers [12][13][14] at different moments sustaining the importance and the permanent actuality of the subject.

3. Marangoni effect and instabilities induced in some refining steel systems

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:

$$\tau_s = \frac{d\gamma}{dx} = \frac{\partial\gamma}{\partial c} \frac{dc}{dx} + \frac{\partial\gamma}{\partial T} \frac{\partial T}{\partial x} + \frac{\partial\gamma}{\partial \psi} \frac{d\psi}{dx} \quad (1)$$

where: γ is superficial tension of the fluid taken into consideration; c – concentration of the superficial active element; T – temperature; ψ – electric potential, when is applied as external action; x – direction on which is estimated or computed the respective gradient of the superficial tension, or the surface tension gradient is acting.

The systems are not usually under the influence of an external electric field and in this case the third term is missing.

The total variation of the superficial tension, due to all factors, as shown in the relation (1), at interface or on the liquid surface, on the direction x , represent a surface tension τ_s .

Systems steel-slag and steel – inclusion are of outmost importance for steel refining to obtain high levels of purity in non-desired elements, like oxygen and sulphur, also non-metallic inclusions. In an earlier paper [16], an extend qualitative analysis of the Marangoni effect in steel was presented.

When the Marangoni effect is the result of the concentration gradients, it is nominated as solutal Marangoni effect and is a direct result of mass transfer between liquid phases or can be an indirect result of buoyancy or of another kind of convection as they are forced flow, heat transfer, temperature gradients. The Marangoni effect is called also as effect of thermocapillarity, or shortly thermocapillarity when it appears as a consequence of the temperature gradients, these last being the results of the heat transfer processes, as well as mass transfer processes, involving enthalpy changes, or also other kinds of natural or forced flow.

Taking into account the existence of large spaces at interface liquid steel-slag strongly stirred by inert gas bubbling, where either the temperature

gradient is nil, in a thin surface layer, or is of a limited small magnitude, it remains of a major importance the solutal Marangoni effect and the associated convection to be analyzed. To evaluate the possibilities of interfacial instability producing usually are used criteria as Marangoni number Ma, frequently presented in the form:

$$\text{Ma} = \frac{\left(-\frac{\partial\gamma}{\partial c}\right)c_0 H}{\mu D} \quad (2)$$

Where: $\partial\gamma/\partial c$ is the variation of the surface tension upon concentration of the chemical element affecting the surface tension; in other cases the variation of the interfacial tension is taken into consideration; c_0 is the characteristic concentration; H – is characteristic length; D – is the diffusion coefficient of the solute in the phase taken into account; μ – is the dynamic viscosity.

4. Possibilities to compute some factors of the solutal Marangoni effect Marangoni number

Until now, according to a wide range of scientific publications, there is not a stable value of the superficial tension of pure iron at temperatures around 1873K. Also, derived from the above reason, there are different relations of the superficial tension dependence of Fe-O and Fe-S solutions on the solute concentration, separately and in the same time. The relevance of the numerical data, regarding different factors of magnitude of the Marangoni effect, computed when active refining processes take place, also the evaluation of instabilities and dynamic effects at the steel-slag and steel inclusion interfaces are of outmost importance, but also are very sensitive to the representatively of the relations used in these calculations.

The quantitative aspects regarding the magnitude of the surface stress τ_s and Ma number can be obtained from obtained data and relations showing the dependence of the surface tension on concentration and temperature.

A such relation is the following:

$$\gamma = 1.936 - 0.00051(T - 1808) - 0.28 \ln(1 - 170[\%O]) - 0.2 \ln(1 - 330[\%S]) \quad (3)$$

obtained in paper [15], based on compilation data from many papers and accepted because is valid in the range of T=1800-1900K. The contents of oxygen and sulphur are in mass%.

At the temperature 1811K, values of the surface tension $\gamma = 1.931 \text{ N/m}$ and of the coefficient of

$$\text{temperature} \quad \frac{\partial\gamma}{\partial T} = 0.000455 \quad \text{N/m} \cdot \text{K} \quad \text{were}$$

established in the paper [17] based on the configurationally energy model and this is the reason of taking into account of the nominated relation (3) despite the fact that there are other several relations of the same acceptance in the specific literature. A special reason of the acceptance of this data is that they are established using the method of the levitated drop which is a dynamic one, being closer as conditions to the practice of steel refining, where there is a permanent flow of the liquid phases.

Of a particular importance is also the interfacial tension liquid steel – nonmetallic inclusion and liquid steel-slag. For interfacial tension iron (liquid)- Al_2O_3 inclusion is proposed the relation [15]:

$$\begin{aligned} \gamma_{\text{Fe-Al}_2\text{O}_3} = & 1.128 - 10^{-4} T - [1.936 - 0.00051(T - 1808) - \\ & - 0.28 \ln(1 + 170[\%O]) - 0.2 \ln(1 + 330[\%S])] \cdot \\ & \cdot \cos[132 - 6.3 \ln(1 + 400[\%O]) - 0.63 \ln(1 + 640[\%S])] \end{aligned} \quad (4)$$

Based on the selected relations some quantitative surface and interfacial effects can be established in the deoxidization and the desulphurization of the steel under refining slag.

The values of Ma number in the solutal Marangoni effect can be computed using the before mentioned relations to which is necessary to add also values or form of dependence for the solute element. The problem is very delicate but, at least roughly, could be used relation (5), proposed by the authors[18] to compute the solute diffusivity of gases oxygen and nitrogen in liquid metals:

$$D_{i-\text{Fe}} = (0.2BRd_{\text{Fe}}^3 / d_i) [(T/V)(V - V_0) / V_0] \quad (5)$$

where: $D_{i-\text{Fe}}$ is diffusion coefficient of the solute i in liquid solvent Fe ; d_{Fe} – Goldschmidt diameter of the solvent Fe ; d_i – atomic diameter of the solute i (gas);

V_0 – atomic volume of the solvent Fe corresponding to the state of zero Fluidity (equivalent to the state of infinite viscosity);

$V_{0,\text{Fe}} = 7.05 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$; V - atomic volume of the liquid solvent Fe ; T - absolute temperature; B - characteristic constant of the liquid metal solvent introduced in the fluidity equation by Hidegrand [19] and for Fe the value is $B = 2.04$.

From the same paper [19] for consistency of data used in computation of the value of viscosity, we have $\mu_{\text{Fe}} = 4.9 \times 10^{-3} \text{ Nm}^{-2} \text{ s}$ and it is given for a temperature when $V/V_0 = 1.1$.

From international tables of fundamental values of elements $d_{\text{Fe}} = 2.8 \times 10^{-10} \text{ m}$, $d_{\text{O}} = 1.2 \times 10^{-10} \text{ m}$, $d_{\text{S}} = 2 \times 10^{-10} \text{ m}$.

4. Conclusions

The combined efforts made in different fields of research and their published results are of nature to allow numeric computations and to get quantitative information about the magnitude of solutal Marangoni effect, Marangoni number, also to evaluate some aspects of the dynamics of the surface processes during refining under slag as deoxidization and desulphurization, including growing and removal of the non metallic inclusions of alumina.

These quantitative data are necessary to clarify better some fine aspects regarding touching and keeping of the high levels of purity and cleanness, necessary to obtain the maximum of performance in low alloyed, HSLA and other steel grades, acting to control and to minimize adverse effects, exerted by those before mentioned factors, in different stages of their processing in liquid state. For ultra fine grain steels and nano-scale driven formation structures in steels, the control of liquid steel dynamics on active surfaces, especially in the final stage of refining treatments, is definitory.

The selected relations, combined with others, regarding similar aspects in refining slag will permit a more complete estimation of the control and benefic aspects at industrial plant scale.

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